



U.S. Department of Interior
U.S. Geological Survey

Composition of crude oil and natural gas produced from 14 wells in the
Lower Silurian "Clinton" sandstone and Medina Group,
northeastern Ohio and northwestern Pennsylvania

R. C. Burruss¹

and

R. T. Ryder¹

Open-File Report 03-409

This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards and stratigraphic nomenclature. Any use of trade names is for descriptive purposes only and does not imply endorsement by the USGS.

¹ U.S. Geological Survey, Reston, Virginia 20192

CONTENTS

	Page
Introduction.....	1
Sample Locations.....	3
Sampling and Analytical Methods.....	4
Results.....	5
Natural gases.....	5
Crude oils.....	7
Preliminary Conclusions.....	8
Natural gases.....	8
Crude oils.....	10
Acknowledgements.....	13
References Cited.....	13

ILLUSTRATIONS

	Page
Figure 1. Map of the Lower Silurian regional oil and gas accumulation showing the location of the study area and regional cross sections A-A' and D-D'	18
Figure 2. Correlation chart of Lower Silurian and adjoining strata, northeastern Ohio, northwestern Pennsylvania, and central Pennsylvania showing the interval of the Lower Silurian regional oil and gas accumulation.....	19
Figure 3. Map showing the well locations in Geauga and Trumbull Counties, Ohio, and Mercer and Butler Counties, Pennsylvania, where oil and (or) gas was sampled for the investigation.....	20

Figure 4.	Schoell (1983) diagram showing the isotopic composition of selected natural gases in the lower Silurian regional oil and gas accumulation.....	21
Figure 5A.	Whole oil gas chromatogram, sample 98OH01B, #2 Patterson.....	22
Figure 5B.	Saturated hydrocarbon fraction gas chromatogram, sample 98OH01B, #2 Patterson.....	23
Figure 5C.	Aromatic hydrocarbon fraction gas chromatogram, sample 98OH01B, #2 Patterson.....	24
Figure 6A.	Whole oil gas chromatogram, sample 98OH02A, #1 Bruno.....	25
Figure 6B.	Saturated hydrocarbon fraction gas chromatogram, sample 98OH02A, #1 Bruno.....	26
Figure 6C.	Aromatic hydrocarbon fraction gas chromatogram, sample 98OH02A, #1 Bruno.....	27
Figure 7A.	Whole oil gas chromatogram, sample 98OH03A, #2 Grandview-Johnson.....	28
Figure 7B.	Saturated hydrocarbon fraction gas chromatogram, sample 98OH03A, #2 Grandview-Johnson.....	29
Figure 7C.	Aromatic hydrocarbon fraction gas chromatogram, sample 98OH03A, #2 Grandview-Johnson.....	30
Figure 8A.	Whole oil gas chromatogram, sample 98OH04A, #1 Detweiler.....	31
Figure 8B.	Saturated hydrocarbon fraction gas chromatogram, sample 98OH04A, #1 Detweiler.....	32
Figure 8C.	Aromatic hydrocarbon fraction gas chromatogram, sample 98OH04A, #1 Detweiler.....	33

Figure 9A.	Whole oil gas chromatogram, sample 98OH05A, #2 Hissa.....	34
Figure 9B.	Saturated hydrocarbon fraction gas chromatogram, sample 98OH05A, #2 Hissa.....	35
Figure 9C.	Aromatic hydrocarbon fraction gas chromatogram, sample 98OH05A, #2 Hissa.....	36
Figure 10A.	Whole oil gas chromatogram, sample 98OH06A, #2 French.....	37
Figure 10B.	Saturated hydrocarbon fraction gas chromatogram, sample 98OH06A, #2 French.....	38
Figure 10C.	Aromatic hydrocarbon fraction gas chromatogram, sample 98OH06A, #2 French.....	39
Figure 11A.	Whole oil gas chromatogram, sample 98OH07A, #3 Griffin.....	40
Figure 11B.	Saturated hydrocarbon fraction gas chromatogram, sample 98OH07A, #3 Griffin.....	41
Figure 11C.	Aromatic hydrocarbon fraction gas chromatogram, sample 98OH07A, #3 Griffin.....	42
Figure 12A.	Whole oil gas chromatogram, sample 98OH08, #1 Bates...	43
Figure 12B.	Saturated hydrocarbon fraction gas chromatogram, sample 98OH08, #1 Bates.....	44
Figure 12C.	Aromatic hydrocarbon fraction gas chromatogram, sample 98OH08, #1 Bates.....	45
Figure 13A.	Whole oil gas chromatogram, sample 98PA02, #6 Weber..	46
Figure 13B.	Saturated hydrocarbon fraction gas chromatogram, sample 98PA02, #6 Weber.....	47
Figure 13C.	Aromatic hydrocarbon fraction gas chromatogram, sample 98PA02, #6 Weber.....	48

Figure 14A.	Whole oil gas chromatogram, sample 98PA05A, #8 Oris...	49
Figure 14B.	Saturated hydrocarbon fraction gas chromatogram, sample 98PA05A, #8 Oris.....	50
Figure 14C.	Aromatic hydrocarbon fraction gas chromatogram, sample 98PA05A, #8 Oris.....	51
Figure 15A.	Whole oil gas chromatogram, sample 98PA06A, #2 Gibson.....	52
Figure 15B.	Saturated hydrocarbon fraction gas chromatogram, sample 98PA06A, #2 Gibson.....	53
Figure 15C.	Aromatic hydrocarbon fraction gas chromatogram, sample 98PA06A, #2 Gibson.....	54
Figure 16.	Plot of pr/nC17 vs. ph/nC18 for “Clinton”/ Medina oils and Utica Shale bitumen extracts.....	55
Figure 17.	Plot of $\delta^{13}\text{C}$ distributions in the saturated and aromatic hydrocarbon fractions for “Clinton”/Medina oils and Utica Shale bitumen extracts.....	56
Figure 18A.	Terpane mass fragmentogram, m/z 191.180, sample 98PA02, #6 Weber.....	57
Figure 18B.	Sterane mass fragmentogram, m/z 217.1956 sample 98PA02, #6 Weber.....	58

TABLES

	Page
Table 1. Wells sampled for gas and oil in northeastern Ohio and northwestern Pennsylvania.....	59
Table 2A. Molecular and isotopic composition of gas samples.....	60
Table 2B. Molecular and isotopic composition of gas samples.....	61
Table 3. Properties of the whole crude oil and crude oil fractions.....	62
Table 4. Properties of the saturated hydrocarbon fraction of the crude oils.....	63
Table 5. Terpane and sterane compounds identified in the saturate fraction of the oil in the #6 Weber well.....	64

Introduction

The Lower Silurian regional oil and gas accumulation was named by Ryder and Zagorski (2003) for a 400-mi-long by 200-mi-wide hydrocarbon accumulation in the central Appalachian basin of the eastern United States and Ontario, Canada (Figure 1). The dominant reservoirs in this regional accumulation are the “Clinton” sandstone, Medina Group sandstones, and Tuscarora Sandstone of Early Silurian age (Figure 2). The basin-center gas (continuous) part of this regional Silurian accumulation contains an estimated 30 trillion cubic feet (TCF) of recoverable gas and covers an area that extends across western Pennsylvania, eastern Ohio, and western West Virginia (Gautier and others, 1995; Ryder, 1998). This part of the accumulation occurs in rocks of low permeability, usually 0.1 millidarcies (md) or less, downdip of more permeable, water-saturated rocks. A conventional part of the accumulation with hybrid features of a basin-center accumulation lies updip from the basin-center gas (Ryder, 1998; Ryder and Zagorski, 2003). This hybrid-conventional part of the regional accumulation follows a pre-1980s production trend that extends from Ontario, Canada, through western New York, northwestern Pennsylvania, and central Ohio (Figure 1).

In the basin-center part of the regional accumulation, individual wells ultimately produce on the order of 50 to 450 million cubic feet (MMCF) of natural gas. In addition to gas, many wells produce variable amounts of brine and crude oil. The gas-to-fluid ratio is variable but generally high, on the order of 50,000 to 500,000 standard cubic feet (SCF) of gas per barrel of oil or brine. The amount of oil and brine produced affects the economics of individual wells because of the cost incurred to dispose of the brine or the

value added through the sale of oil. In general, the best gas producers are those wells that produce the least oil and brine.

We are investigating the geochemistry of the gas and co-produced oil to better understand the origin of the hydrocarbons within the Lower Silurian regional accumulation. This report documents 12 gas samples and 11 oil samples from 14 wells producing from the “Clinton” sandstone and Grimsby/Whirlpool Sandstones in northeastern Ohio and northwestern Pennsylvania. The samples from Ohio were collected in Geauga and Trumbull Counties and those from Pennsylvania were collected in Butler and Mercer Counties. This investigation supplements a previous data set of 10 oil samples and 3 gas samples collected from the “Clinton” sandstone in Trumbull County (Barton, Burruss, and Ryder, 1998; Burruss and Ryder, 1998).

Other published analyses of crude oils and natural gases from Silurian-age reservoirs in the Appalachian basin include those by Barker and Pollock (1984), Cole, Drozd, and others (1987), Drozd and Cole (1994), Jenden, Drazan, and Kaplan (1993), Laughrey and Baldassare (1998), Obermajer, Fowler, and Snowdon (1998), and Powell, Macqueen, and others (1984). Cole, Drozd, and others (1987) recognized two groups of oils in Silurian reservoirs in Ohio. One group of oil, they suggested, was generated from marine black shale of Devonian age and the other group was generated from marine black shale of Ordovician age. Most likely, oil in the Lower Silurian “Clinton” sandstone was generated from the Ordovician black shale (Drozd and Cole, 1994; Ryder, Burruss, and Hatch, 1998). Devonian black shale is a less likely source for the “Clinton” oils because the 700-to-1,000-ft-thick Upper Silurian Salina Group, with evaporite beds, is located between them (Figure 1). Molecular and isotopic data on natural gas from

Silurian reservoirs in western and central Pennsylvania (Laughrey and Baldassare, 1998) and western New York (Jenden, Drazan, and Kaplan, 1993) are less diagnostic for identifying source rock than geochemical parameters measured in oil samples. However, the general conclusion of work to date on “Clinton”/Medina/ Tuscarora gases is that they were derived from thermally mature, marine organic matter, probably in strata older than the Silurian.

Sample Locations

The wells sampled for this investigation follow a northwest-southeast trend that is subparallel to the dip of the basin and crosses the approximate boundary between basin-center and hybrid-conventional parts of the Lower Silurian regional accumulation (Figures 1, 3). In general, those wells east of Mosquito Creek Lake in central Trumbull County are located in the basin-center part of the Lower Silurian regional accumulation whereas those wells west of Mosquito Creek Lake are located in the hybrid-conventional part (Figure 3). All wells sampled are within 5 miles of cross section D-D’ that shows the stratigraphic and depositional character of the “Clinton” sandstone and Medina Group (Keighin, 1998) (Figure 3). Cross section A-A’ (Ryder, 2000), which connects with cross section D-D’ in Mercer County, is located 5 to 10 miles from the wells sampled in southeastern Mercer and northwestern Butler Counties (Figure 3). Also located in Figure 3 are 10 wells in Trumbull County for which oil and gas analyses have been reported by Burruss and Ryder (1998). Selected information on the wells sampled for this investigation is listed in Table 1.

Sampling and Analytical Methods

Most oil and gas samples were obtained, with the assistance of operating company field personnel, from the wellhead or the oil and gas separator of individual wells. One oil sample was taken from the stock tank at the well site. Gas was sampled at the pressure gauge port on the production tubing using evacuated stainless steel cylinders supplied by Isotech Laboratories, Inc. Oil was sampled, where possible, at the drain for the fluid-level sightglass on the oil and gas separator. The oil is initially saturated with gas at the separator pressure and foams from exsolution of the gas as it exits the sightglass drain. One oil sample was bailed from the stock tank.

All samples were analyzed by standard methods. Natural gas samples were analyzed at Isotech Laboratories, Inc., Champaign, Illinois, for molecular composition by gas chromatography and for stable isotopic composition by isotope ratio mass spectrometry. Carbon isotopic composition was determined for methane (C_1), ethane (C_2), propane (C_3), and iso-butane (C_4). Also, hydrogen isotopic composition was determined for methane and nitrogen isotopic composition was determined for molecular nitrogen. Carbon isotope ratios are reported in standard per mil deviation relative to the Peedee belemnite standard (PBS), and hydrogen isotope ratios are reported relative to standard mean ocean water (SMOW) for both gases and oils. Nitrogen isotope ratios are reported relative to atmospheric nitrogen.

Crude oils were analyzed by the U.S. Geological Survey (Denver, Colorado). API gravity of the oils was determined gravimetrically. Oils were fractionated by dilution in *n*-heptane to remove asphaltenes. A concentrate of the solution was further fractionated by column chromatography on silica gel by selective elution with heptane,

benzene, and benzene-methanol (1:1 v/v) to collect the saturated hydrocarbon, aromatic hydrocarbon, and resin (nitrogen-, sulfur-, and oxygen- [NSO] compounds) fractions, respectively. The carbon stable isotope composition of an aliquot of the saturated and aromatic hydrocarbon fractions was determined on a Micromass Optima isotope ratio mass spectrometry system.

Gas chromatography of the whole oil, and the saturated and aromatic hydrocarbon fractions, was performed with a Hewlett/Packard Model 6890 (HP6890) gas chromatograph with a 60 m x 0.32 mm x 0.25 μ m DB-1 fused silica capillary column and a FID detector. The oven was programmed from 50 to 330°C at 4.5°C/min and held isothermal at 330°C for 15 min with helium carrier gas flow at 35 cm/sec. Gas chromatography-mass spectrometry (GCMS) of the saturated hydrocarbon fraction of one oil was performed with a HP6890-JEOL GCMate system in selective ion monitoring mode to identify steranes and terpanes in the fraction.

Results

Natural gases: The molecular and isotopic composition of natural gas from twelve wells is presented in Tables 2A and 2B. All twelve gases are rich in methane, between 76 and 90 mole %, with low concentrations of hydrocarbons that have more than four carbon atoms. All samples contain a trace of helium and 2.01 to 4.55 mole % nitrogen. Eight of the twelve wells contain a trace of hydrogen. These gas compositions are consistent with gas compositions reported for the “Clinton” sandstone in Ohio by the U.S. Bureau of Mines (Moore, 1982).

The carbon isotopic composition of methane, ethane, propane, and *n*-butane in the samples ranges from about 7 to 12 per mil for each component. In eight of twelve wells,

the carbon isotopic composition of methane, ethane, propane, and *n*-butane (where analyzed) become respectively heavier as normally expected (Chung, Gormly, and Squires, 1988) whereas, in four wells, the carbon isotopic composition of methane, ethane, propane, and *n*-butane (where analyzed) show several combinations of reversal in the normal trend (see #5 Brown; table 2B). The variation in the hydrogen isotopic composition of methane is about 50 per mil and the variation in the nitrogen isotopic composition ranges is about 4 per mil. The carbon dioxide content in the samples was so low, 0.04 mole % or less, that the carbon isotopic composition of this constituent could not be determined.

Judging from their isotopic location on a Schoell (1983) diagram (Figure 4), “Clinton”/Medina natural gases from this study and from Burruss and Ryder (1998) are thermogenic in origin. The $\delta^{13}\text{C}$ methane and δD methane values define a straight line that indicates that the gases become isotopically heavier with depth of production (Figure 4). For example, $\delta^{13}\text{C}$ methane values range from -41.98 in the #2 Patterson well (~3,600 ft to the gas production) near the northwest end of section D-D’ to -33.97 in the #2 Mathews well (~6,570 ft) near the southeast end. Isotopic compositions of additional Lower Silurian gases from northwestern Pennsylvania (Laughrey and Baldassare, 1998) and Lower Silurian gases from New York (Jenden, Drazan, and Kaplan, 1993) also fit the trend defined in Figure 4. Natural gases in the basin-center part of the regional accumulation are differentiated from natural gases in the hybrid-conventional part based on their position relative to the $\delta^{13}\text{C}$ methane = -37.0 value (Figure 4).

Crude oils: Bulk parameters and selected molecular parameters of the crude oils are listed in Table 3. The API gravity of 8 of the 11 samples is 40° or greater. One of the 3 exceptions, the No. 6 Weber well with an API gravity of 39.9°, was bailed from the top of the stock tank instead of being collected at the separator. The oils are uniformly high (84 to 92 wt. %) in saturated hydrocarbons with 12% or less of aromatic hydrocarbons. Carbon isotopic compositions of the saturated and aromatic hydrocarbon fractions show small ranges of 0.8 per mil and 1.0 per mil, respectively.

Gas chromatograms of the whole oil, saturated hydrocarbon, and aromatic hydrocarbon fractions for samples from the 11 wells are shown in Figures 5A, 5B, 5C, respectively, through Figures 15A, 15B, 15C. The saturated hydrocarbon gas chromatograms have similar characteristics to “Clinton” oils reported by Cole, Drozd, and others (1987). Molecular parameters derived from the gas chromatograms of the saturated hydrocarbon fractions are listed in Table 4. All whole-oil gas chromatograms of the saturated hydrocarbon fraction, except the one from the #6 Weber well, show a full spectrum of *n*-alkanes from *n*-C₁₀ to *n*-C₃₀₊. The whole oil chromatogram for the sample from the #6 Weber well shows depletion in the low carbon number range (<*n*-C₁₀) suggesting evaporative loss of the light ends. Two types of *n*-alkane distributions and one intermediate type are recorded by the saturated fraction gas chromatograms. Including the depleted #6 Weber sample, six of the eleven chromatograms show a broad spectrum of *n*-alkanes whose peak heights progressively diminish toward the higher carbon numbers (Figure 8B); two chromatograms have a bimodal distribution of *n*-alkanes that peak at about *n*-C₁₄ and *n*-C₂₄ (Figure 6B); and three chromatograms show a broad spectrum of *n*-alkanes whose peak heights progressively diminish toward the

higher carbon numbers but show a secondary peak at *n*-C₂₄ (Figure 11B). Both types of *n*-alkane distribution show a modest odd-carbon preference and the presence of isoprenoids. The pristane/phytane (pr/ph) ratios listed in Table 4 range from 1.31 to 2.01.

Crude oils from “Clinton”/Medina reservoirs in this study and in Burruss and Ryder (1998) are characterized by pr/*n*-C₁₇ and ph/*n*-C₁₈ values that vary broadly with their depth of production (Figure 16). Major exceptions are sample 14 (#6 Weber) that is grouped with oils produced from much shallower depths and sample 6 (#3 Griffin) that is grouped with oils produced from much greater depths (Figure 16). Moreover, carbon isotopic compositions of the saturated and aromatic fractions of the oils, in general, become heavier with depth (Figure 17). Basin-center and hybrid-conventional parts of the regional accumulation can be largely differentiated on the basis of trends shown in Figures 16 and 17.

Mass fragmentograms from gas chromatography-mass spectrometry (GCMS) of the crude oil samples indicate the presence of biomarkers although many are barely visible because of their low signal-to-noise ratio. Surprisingly, the best fragmentograms are from the depleted oil in the #6 Weber well. Terpane (m/z 191) and sterane (m/z 217) fragmentograms of this oil are shown in Figures 18A and 18B, respectively.

Preliminary Conclusions

Natural gases: The striking distribution of $\delta^{13}\text{C}$ methane vs. δD methane compositions is clearly a function of the thermal maturity of the gases (Figure 4). In addition, given the orderly increase toward heavier isotopes with depth, there appears to have been very little mixing of the gases in the “Clinton”/Medina reservoirs after entrapment. Also, these data

imply a common source rock for the gases. Several explanations are possible for the isotopic distributions shown in Figure 4. First, gases may have been introduced to Lower Silurian reservoirs from a distant source, became trapped, and then thermally modified, *in situ*, as the reservoirs gradually achieved maximum burial. Secondly, gases may have been introduced from a local source rock and then trapped before it was allowed to migrate laterally. In these two models, the gases had minimal mobility during late-stage basin uplift. A third model suggests that the isotopic character of the gases is a late-stage, leakage/fractionation phenomenon whereby the volume of the escaped gas is directly related to the thickness of overburden. Therefore, isotopic compositions would be heaviest in gases having the greatest overburden thickness.

Furthermore, conodont alteration index (CAI) isograds for Middle Ordovician carbonate rocks (Repetski and others, 2002; J.E. Repetski and R.T. Ryder, unpubl. data) show a consistently lower thermal maturity value, for a given locality, than that of the gas (Jenden, Drazan, and Kaplan, 1993) (Figure 4). Figure 4 suggests that gases in the “Clinton”/Medina were derived from source rocks having thermal maturity values about 1 to 1.5 vitrinite reflectance equivalence (VRE) (Nöth, 1991) greater than the thermal maturity of the underlying Middle Ordovician strata based on CAI isograds. A similar discrepancy occurs when the thermal maturity of the gases are compared with the thermal maturity of the overlying Lower/Middle Devonian strata based on CAI isograds and vitrinite reflectance (Ro%) isorefectance lines.

The fact that these gases have a significantly higher thermal maturity than the underlying Ordovician and overlying Devonian strata suggests that they migrated from deeper in the basin. Moreover, a Utica Shale source rock is favored over a Devonian

shale source rock because of the shorter migration distance (25 to 50 mi vs. >100 mi) that the Utica requires to account for the observed thermal maturity of the gases. Although these data are most consistent with model 1 for the origin of the gases (medium-range migration with isotopic signatures being set during maximum burial), model 3 (medium-range migration with isotopic signatures being set during late-stage uplift and erosion of the basin) cannot be rejected. Methane $\delta^{13}\text{C}$ > ethane $\delta^{13}\text{C}$ values observed in several natural gases in this study (Table 2B) may have resulted from the mixing of mature and post-mature gases (Jenden, Drazan, and Kaplan, 1993; Laughrey and Baldassare, 1998); however, diffusive leakage of gas through overburden rock (as permitted in model 3) may be an alternate explanation (Laughrey and Baldassare, 1998).

Crude oils: The majority of *n*-alkane distributions for whole-oil gas chromatograms in this investigation (Figures 6A-13A and 15A) show: 1) a broad spectrum of *n*-alkanes ranging from *n*-C₁₀ through *n*-C₃₅, 2) modest odd-carbon preference in the *n*-C₁₅ through *n*-C₁₉ range, and 3) the presence of isoprenoids pristane and phytane. The major exception to the rule is the oil from the #6 Weber well (Figure 13A) which has an incomplete spectrum of *n*-alkanes (*n*-C₁₀ and *n*-C₁₁ are nearly depleted) and lacks odd-carbon predominance in the *n*-C₁₅ through *n*-C₁₉ range. As noted earlier, the characteristics of the #6 Weber oil were probably caused by evaporative loss during sampling and storage.

The oils analyzed in this investigation have the same basic composition as other oils from the “Clinton” reservoir in Ohio (Cole, Drozd, and others, 1987; Burruss and Ryder, 1998) and oils from Cambrian/Ordovician reservoirs in Ohio (Cole, Drozd, and

others, 1987; Ryder, Burruss, and Hatch, 1998). These basic similarities suggest a common source rock, probably the Middle Ordovician Utica Shale, for the “Clinton” and Cambrian/Ordovician reservoirs (Cole, Drozd, and others, 1987; Ryder, Burruss, and Hatch, 1998). Geochemical and geological evidence are much less convincing for other source rocks such as the Lower/Middle Devonian black shale and Silurian shale/carbonate units (Ryder and Zagorski, 2003).

CAI isograds for Middle Ordovician carbonates gradually increase eastward across the study area from 1.5 to 2.0 (VRE 0.5 to 1) (Repetski and others, 2002; J.E. Repetski and R.T. Ryder, unpubl. data). These isograds are indicative of the “window” of oil and wet gas generation and preservation and, thus, are permissive of local derivation of the oils from the Utica Shale. Also, local oil derivation from the Utica is suggested by the similarity of carbon isotopic distributions in Utica Shale extracts from Coshocton County, Ohio (Figure 3) (depth = 5,600-5,700 ft) and “higher” maturity oils from “Clinton” reservoirs (Figure 17). Moreover, the general eastward (basinward) increase in thermal maturity of the oils, based on $pr/n-C_{17}$ vs. $pr/n-C_{18}$ (Figure 16) and carbon isotopic distributions (Figure 17), suggests that minimal lateral migration of oil had occurred before entrapment.

Oil from the #6 Weber well is anomalous because it is geochemically associated with “lower” maturity oils (Figure 16) and is geologically associated with the CAI 3 isograd (VRE 2.25) (Repetski and others, 2002) that signifies the “window” of dry gas generation and preservation. Either this oil was introduced from a lower maturity source rock such as the overlying Devonian black shale or was locally preserved in a relatively high thermal regime that favored the generation and preservation of dry gas. In contrast,

oil from the #3 Griffin well at a depth of about 3,900 ft is geochemically associated with “higher” maturity oils whose depth of production is approximately 1,000 ft greater (Figures 16 and 17). Possibly this oil migrated into the vicinity of the #3 Griffin well from deeper in the basin, or from a more mature secondary phase of generation that occurred beneath the well, and was trapped next to the lower maturity oil. Additional evidence for the mixing of different several oil types — either caused by a different source rock or thermal maturity regime — is suggested by the bimodal *n*-alkane distributions noted in several oils (see Figure 6B).

The following sequence of events represents one scenario for the origin of the oils: 1) oil generation from the Utica Shale, 2) vertical migration of the oil into the overlying “Clinton”/Medina reservoir, 3) probable entrapment of the oil before significant lateral migration had occurred, and 4) local mixing of oils from disparate thermal regimes during late-stage basin uplift and erosion. This scenario suggests that the crude oils evolved later, and from a more local source, than the natural gases described in the previous section.

Acknowledgements

Rick Liddle, Range Resources, Inc. (now Great Lakes Energy Partners), and Frank Carolas, Atlas Resources, Inc., enthusiastically gave permission and made arrangements for us to sample the wells. Assistance with field sampling was kindly and patiently provided by Earl (Pep) Horning, John Frederick, and Dave Smallwood, Range Resources, Inc. (now Great Lakes Energy partners), and Pete Burns, Atlas Resources, Inc.

References Cited

Barker, J. F., and Pollock, S. J., 1984, The geochemistry and origin of natural gases in southern Ontario: Bulletin of Canadian Petroleum Geology, v. 32, p. 313-326.

Barton, G. L., Burruss, R. C., and Ryder, R. T., 1998, Water quality in the vicinity of Mosquito Creek Lake, Trumbull County, Ohio, in relation to the chemistry of locally occurring oil, natural gas, and brine: U.S. Geological Survey Water-Resources Investigations Report 98-4180, 46 p.

Burruss, R. C., and Ryder, R. T., 1998, Composition of crude oil and natural gas produced from 10 wells in the Lower Silurian "Clinton" sands, Trumbull County, Ohio: U.S. Geological Survey Open-File Report 98-799, 50 p.

Chung, H. M., Gormly, J. R., and Squires, R. M., 1988, Origin of gaseous hydrocarbons in subsurface environments: theoretical considerations of carbon isotope distribution: *Chemical Geology*, v. 71, p. 97-103.

Cole, G. A., Drozd, R. J., Sedivy, R. A., and Halpern, H. I., 1987, Organic geochemistry and oil-source correlations, Paleozoic of Ohio: *American Association of Petroleum Geologists Bulletin*, v. 71, p. 788-809.

Drozd, R. J., and Cole, G. A., 1994, Point Pleasant-Brassfield(!) petroleum system, Appalachian Basin, U.S.A., *in* Magoon, L. B., and Dow, W. G., eds., *Petroleum system — from source to trap*: Tulsa, Oklahoma, American Association of Petroleum Geologists Memoir 60, p. 387-398.

Gautier, D. L., Dolton, G. L., Takahashi, K. I., and Varnes, K. L., eds., 1995, 1995 National Assessment of United States Oil and Gas Resources — Results, methodology, and supporting data: U.S. Geological Survey Digital Data Series DDS-30.

Jenden, P. D., Drazan, D. J., and Kaplan, I. R., 1993, Mixing of thermogenic natural gases in northern Appalachian basin: *American Association of Petroleum Geologists Bulletin*, v. 77, p. 980-998.

Keighin, C. W., 1998, Depositional dip-oriented cross-section through the Lower Silurian "Clinton" sands and Medina Group in northeastern Ohio and western Pennsylvania, US: U.S. Geological Survey Open-File Report 98-500, 1 sheet.

Laughrey, C. D., and Baldassare, F. J., 1998, Geochemistry and origin of some natural gases in the Plateau province of the central Appalachian basin, Pennsylvania and Ohio: American Association of Petroleum Geologists Bulletin, v. 82, p. 317-335.

Lewan, M. D., and Buchardt, B., 1989, Irradiation of organic matter by uranium decay in the Alum Shale, Sweden: *Geochemica et Cosmochimica Acta*, v. 53, p. 1307-1322.

Moore, B. J., 1982, Analysis of natural gases, 1917-1980: U.S Bureau of Mines Information Circular 8870, 1055 p.

Nöth, S., 1991, Die Conodontendiagenese als Inkohlungsparameter und ien Vergleich unterschiedlich sensativer Diagenese-indicatoren am Beispeil von Triassedimenten Nord- und Mitteldeutschlands: *Bochumer geol. U. geotech. Arb.* 37, 169 p., Bochum.

Obermajer, M., Fowler, M. G., and Snowdon, L. R., 1998, A geochemical characterization and a biomarker re-appraisal of the oil families from southwestern Ontario, Canada: *Bulletin of Canadian Petroleum Geology*, v. 46, p. 350-378.

Powell, T. G., Macqueen, R. W., Barker, J. F., and Bree, D. G., 1984, Geochemical character and origin of Ontario oils: *Bulletin of Canadian Petroleum Geology*, v. 32, p. 299-312.

Repetski, J. E., Ryder, R. T., Harper, J. A., and Trippi, M. H., 2002, Thermal maturity patterns (CAI and %Ro) in the Ordovician and Devonian rocks of the Appalachian basin in Pennsylvania: *U. S. Geological Survey Open-File Report 02-302*, 57 p.

Ryder, R. T., 1998, Characteristics of discrete and basin-centered parts of the Lower Silurian regional oil and gas accumulation, Appalachian basin: Preliminary results from a data set of 25 oil and gas fields: *U.S. Geological Survey Open-File Report 98-0216*, 71 p.

Ryder, R. T., 2000, Stratigraphic framework and depositional sequences in the Lower Silurian regional oil and gas accumulation, Appalachian basin: From Jackson County, Ohio, through northwestern Pennsylvania, to Orleans County, New York: *U.S. Geological Survey Miscellaneous Investigations Map I-2726*, 2 sheets, pamphlet, 8 p.

Ryder, R. T., Burruss, R. C., and Hatch, J. R., 1998, Black shale source rocks and oil generation in the Cambrian and Ordovician of the central Appalachian basin, USA: *American Association of Petroleum Geologists Bulletin*, v. 82, p. 412-441.

Ryder, R. T. and Zagorski, W. A., 2003, Nature, origin, and production characteristics of the Lower Silurian regional oil and gas accumulation, central Appalachian Basin, United States: American Association of Petroleum Geologists Bulletin, v. 87, no. 5, p. 847-872.

Schoell, M., 1983, Genetic characteristics of natural gases: American Association of Petroleum Geologists Bulletin, v. 67, p. 2225-2238.

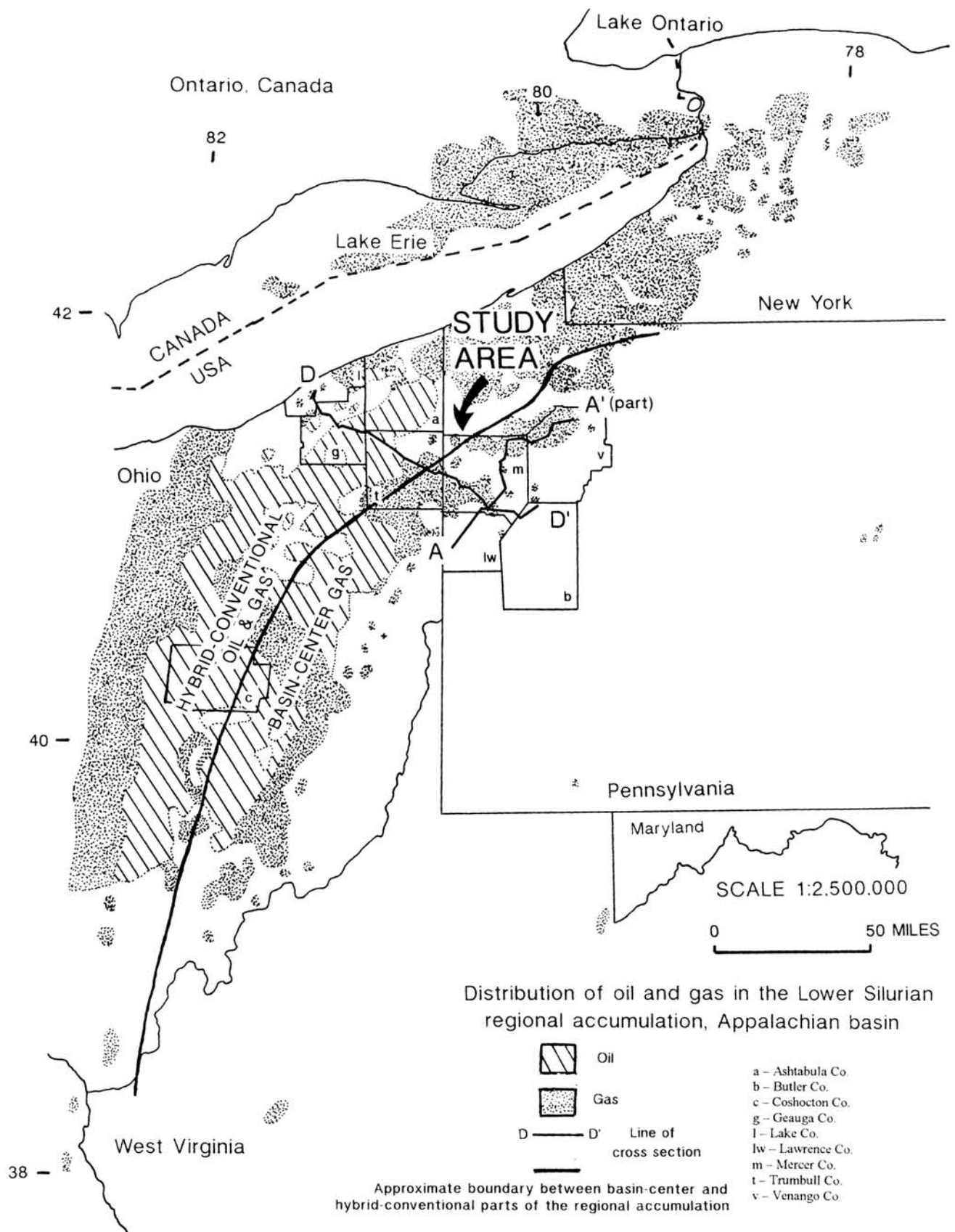


Figure 1. Map of the Lower Silurian regional oil and gas accumulation showing the location of the study area and cross sections A-A' and D-D'.

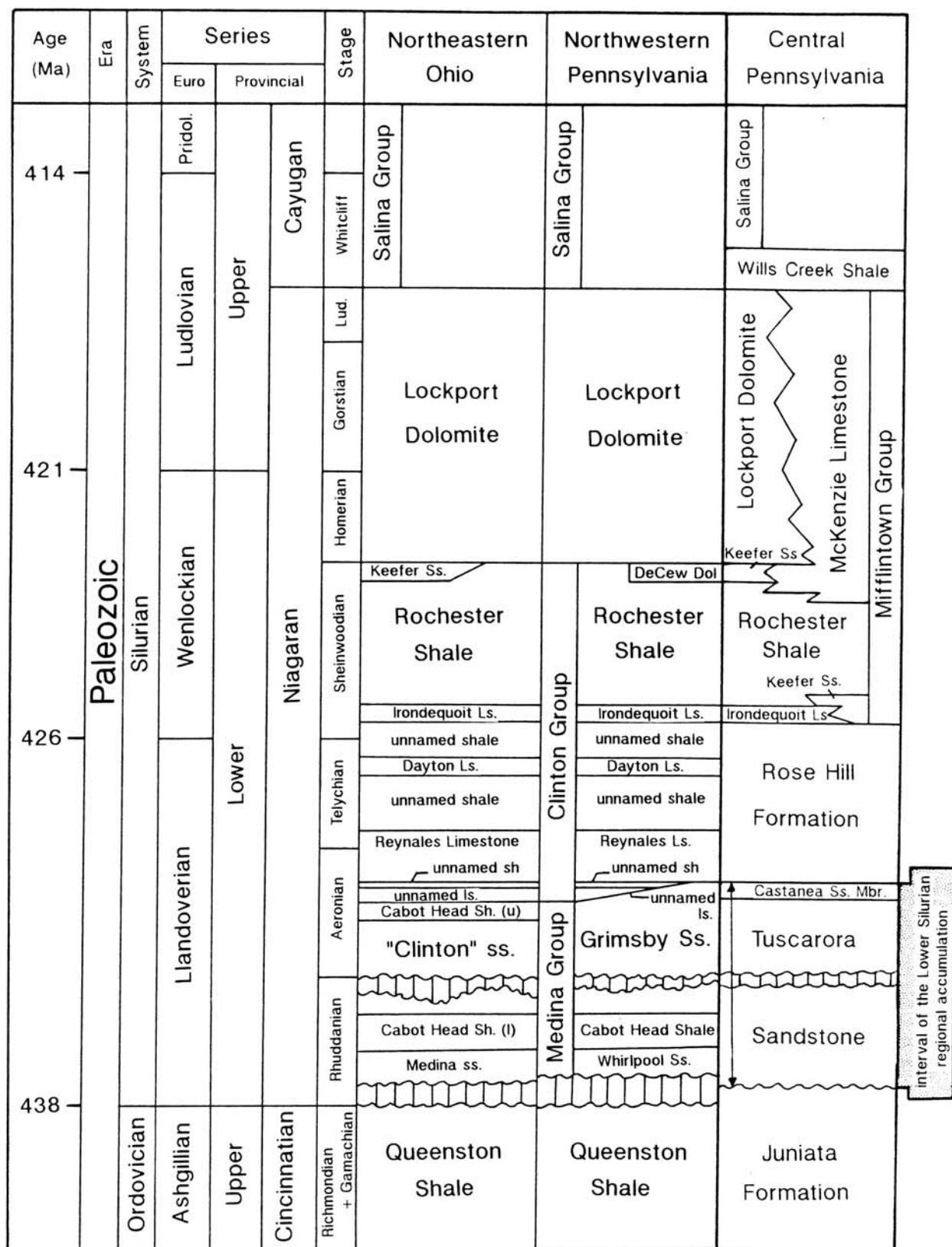


Figure 2. Correlation chart of Lower Silurian and adjoining strata, northeastern Ohio, northwestern Pennsylvania, and central Pennsylvania, showing the interval of the Lower Silurian regional and gas accumulation.

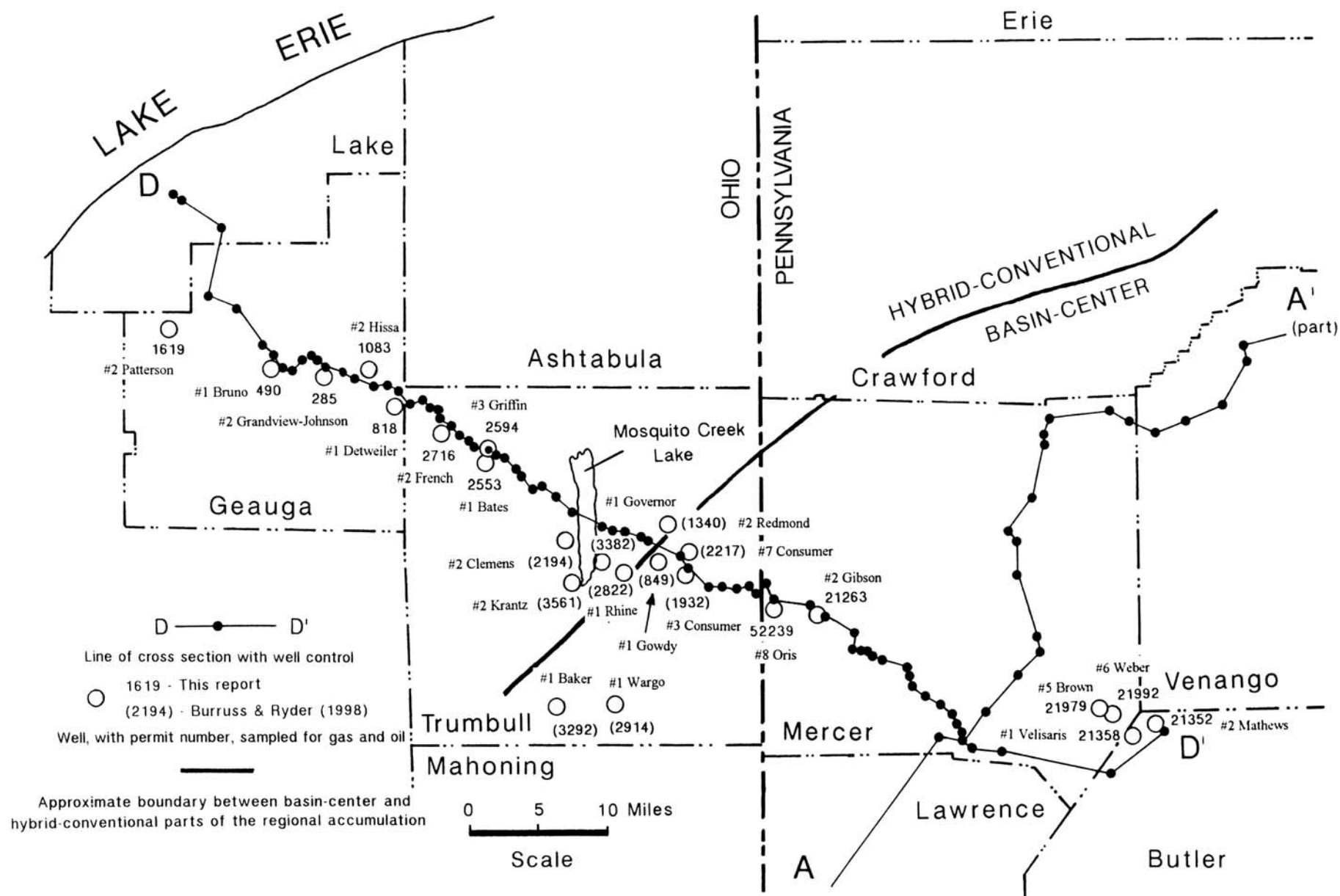


Figure 3. Map of the study area in northeastern Ohio and northwestern Pennsylvania showing well locations in Geauga and Trumbull Counties, Ohio, and Mercer and Butler Counties, Pennsylvania, where oil and (or) gas was sampled for this investigation and the Burruss and Ryder (1998) investigation.

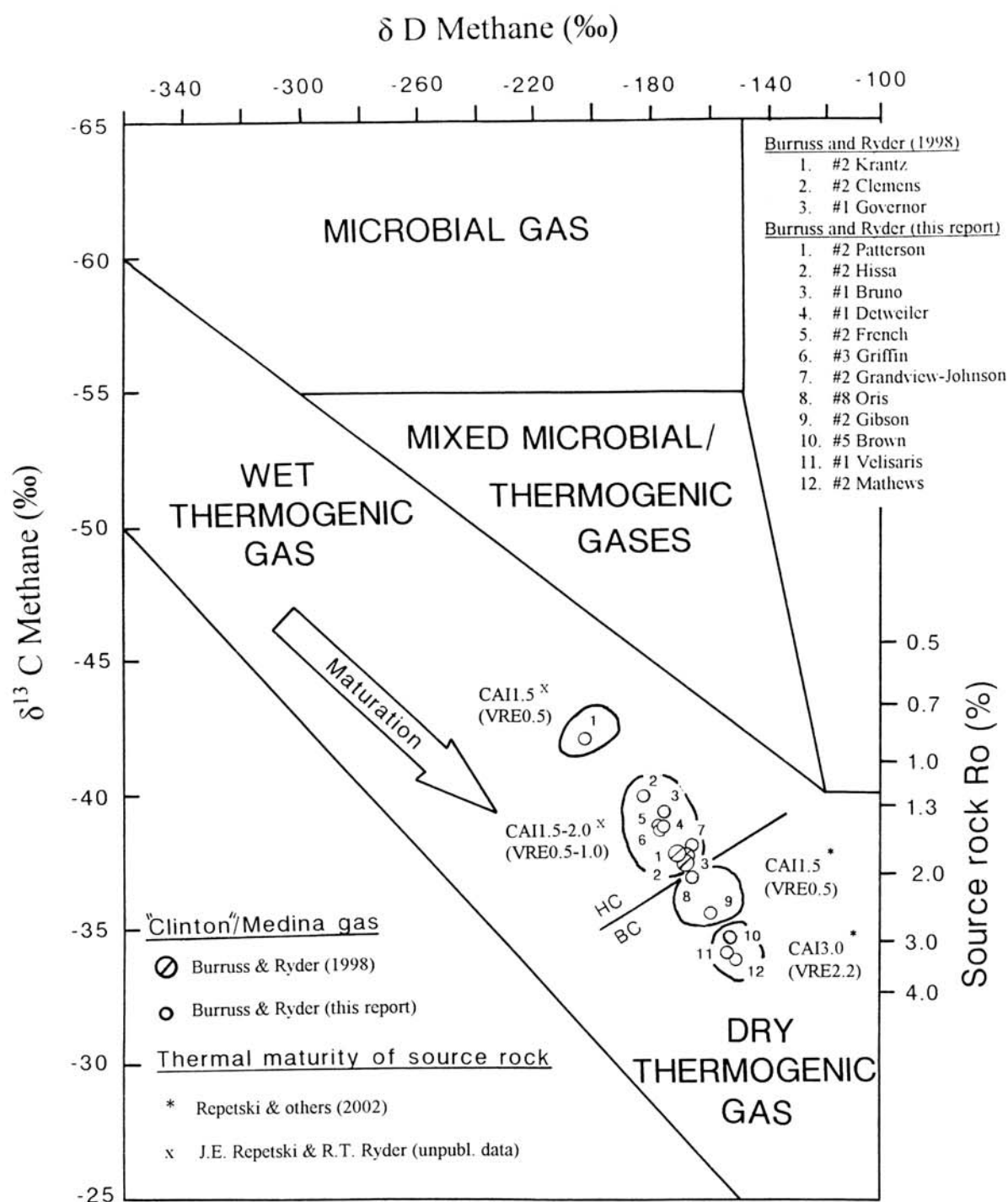


Figure 4. Schoell (1983) diagram showing the isotopic composition of selected natural gases in the Lower Silurian regional oil and gas accumulation. A scale devised by Jenden and others (1993) for estimating the approximate vitrinite reflectance (%Ro) of the source rock that generated the gas is attached to the right side of the diagram. Also shown are the CAI thermal maturity values for Middle Ordovician carbonate rocks located near the proposed Middle Ordovician Utical Shale source rock.

CAI = Conodont alteration index; VRE = Vitrinite reflectance equivalence based on Noth (1991); BC = Basin-center part of the regional accumulation; HC = Hybrid-conventional part of the regional accumulation.

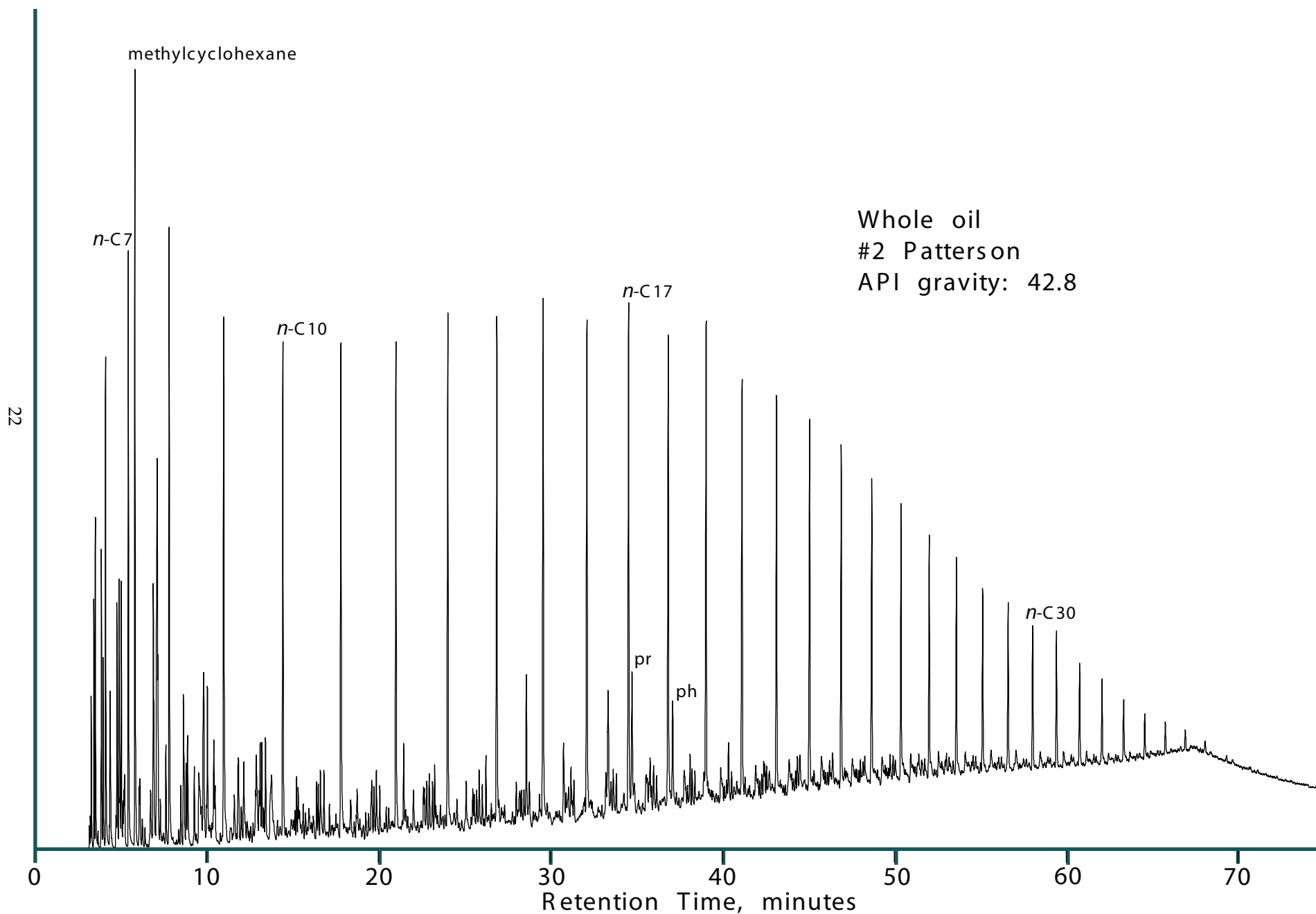


Figure 5A: Whole oil gas chromatogram, sample 98OH01B, #2 Patterson. Selected peak identifications: *n*-CX, normal alkanes where X is the carbon number; pr, pristane; ph, phytane.

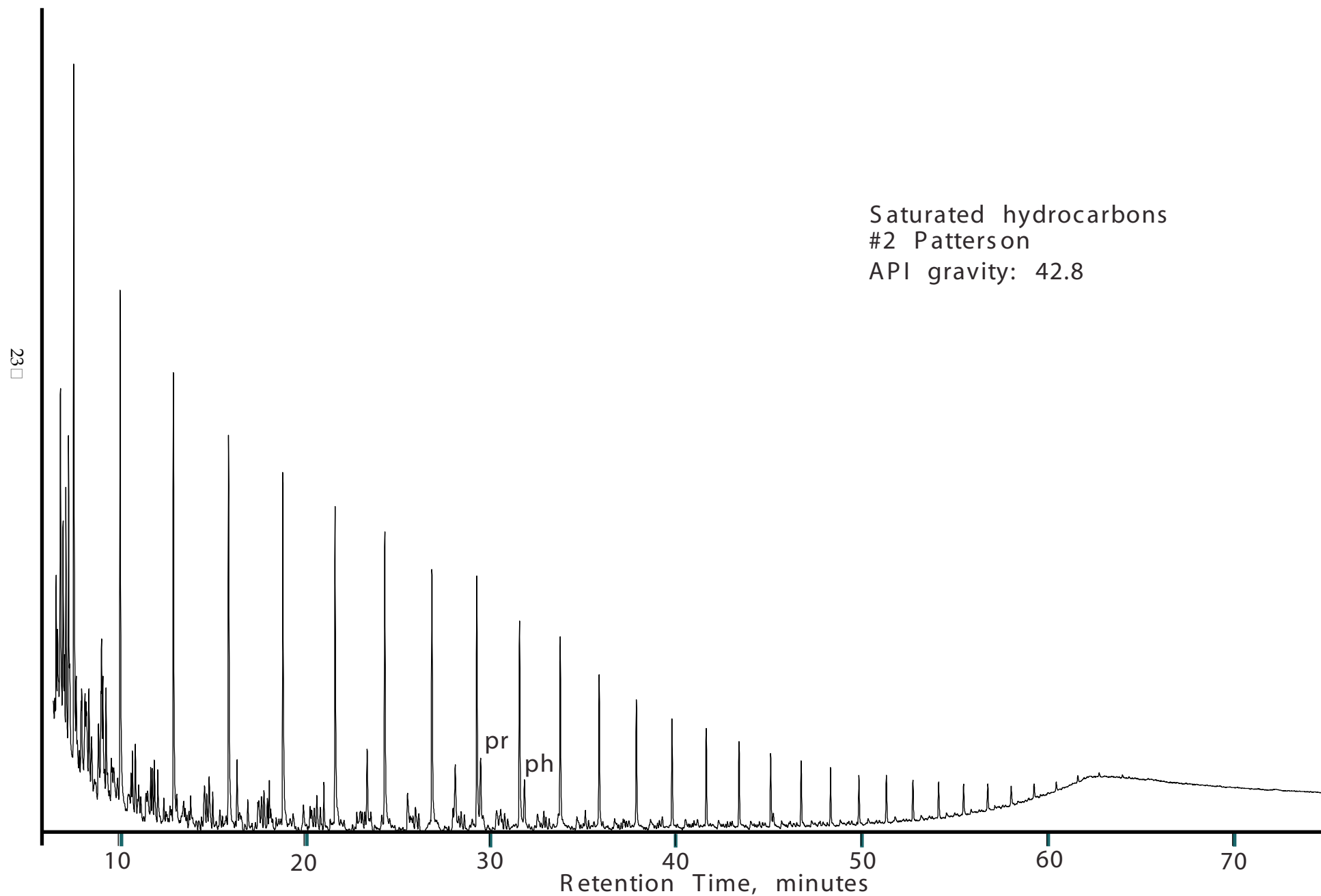


Figure 5B: Saturated hydrocarbon fraction gas chromatogram, sample 98OH01B, #2 Patterson.

Aromatic hydrocarbons
#2 Patterson
API gravity: 42.8

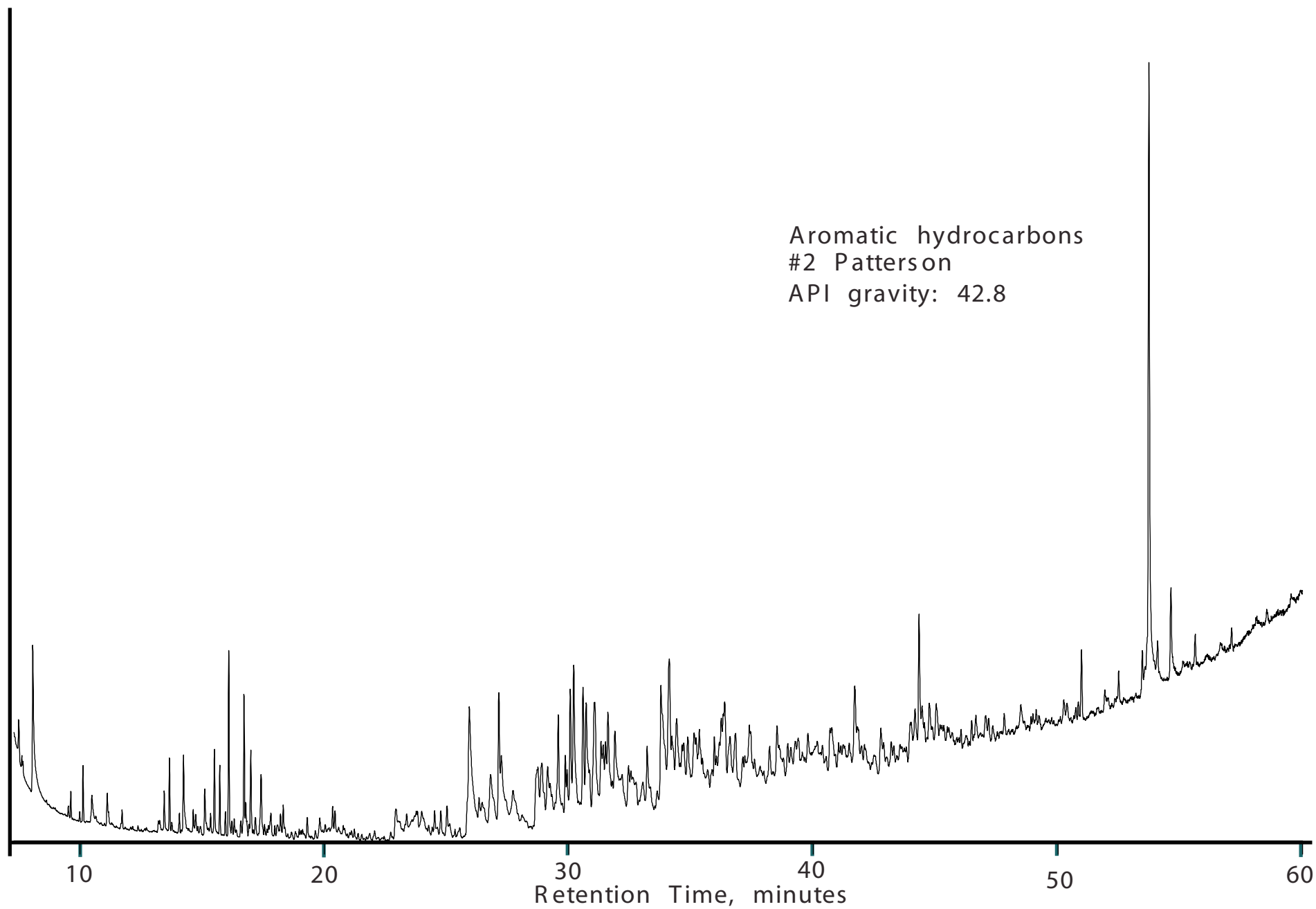


Figure 5C: Aromatic hydrocarbon fraction gas chromatogram, sample 98OH01B, #2 Patterson.

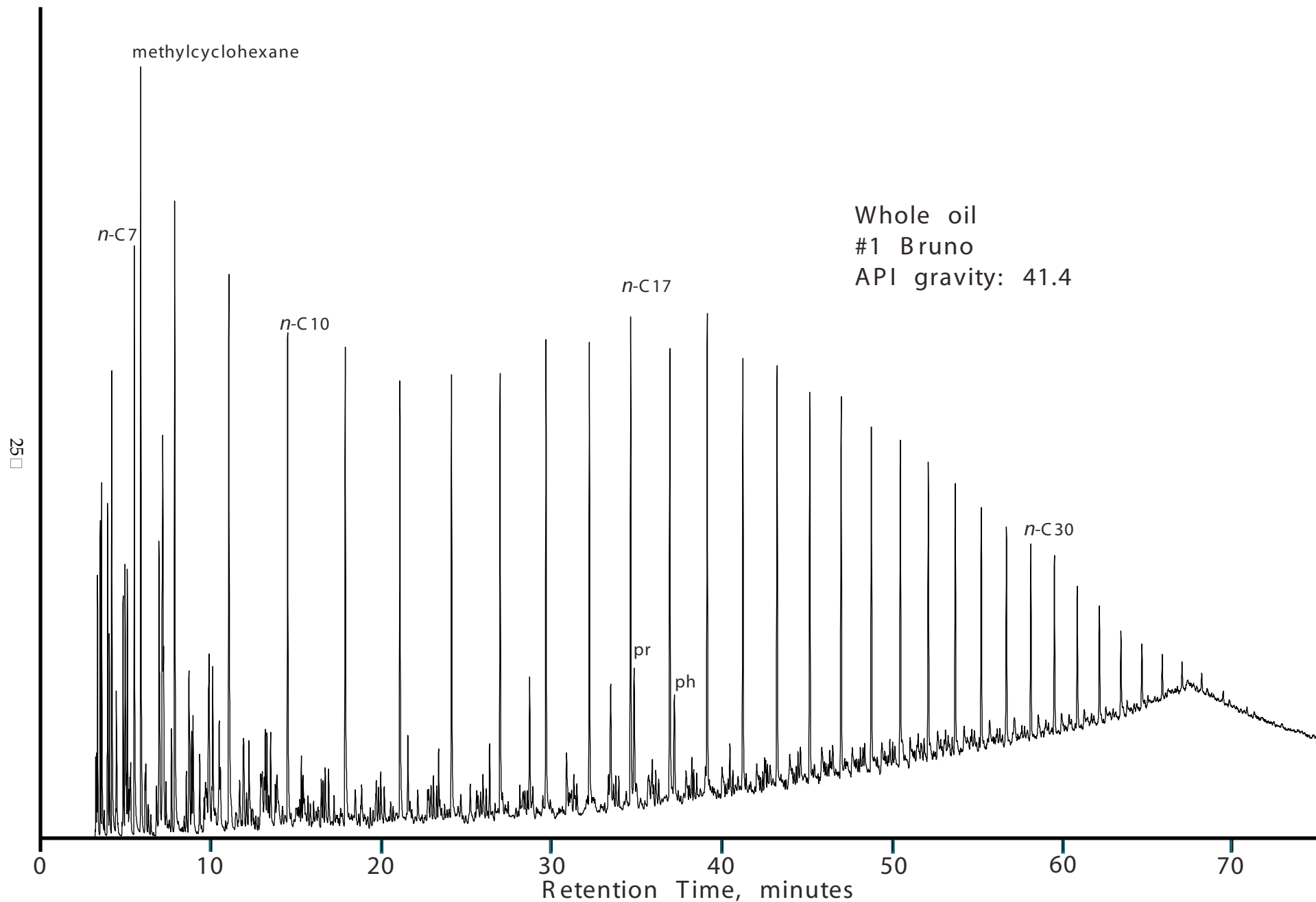


Figure 6A: Whole oil gas chromatogram, sample 98OH02A, #1 Bruno. Selected peak identifications: *n*-CX, normal alkanes where X is the carbon number; pr, pristane; ph, phytane.

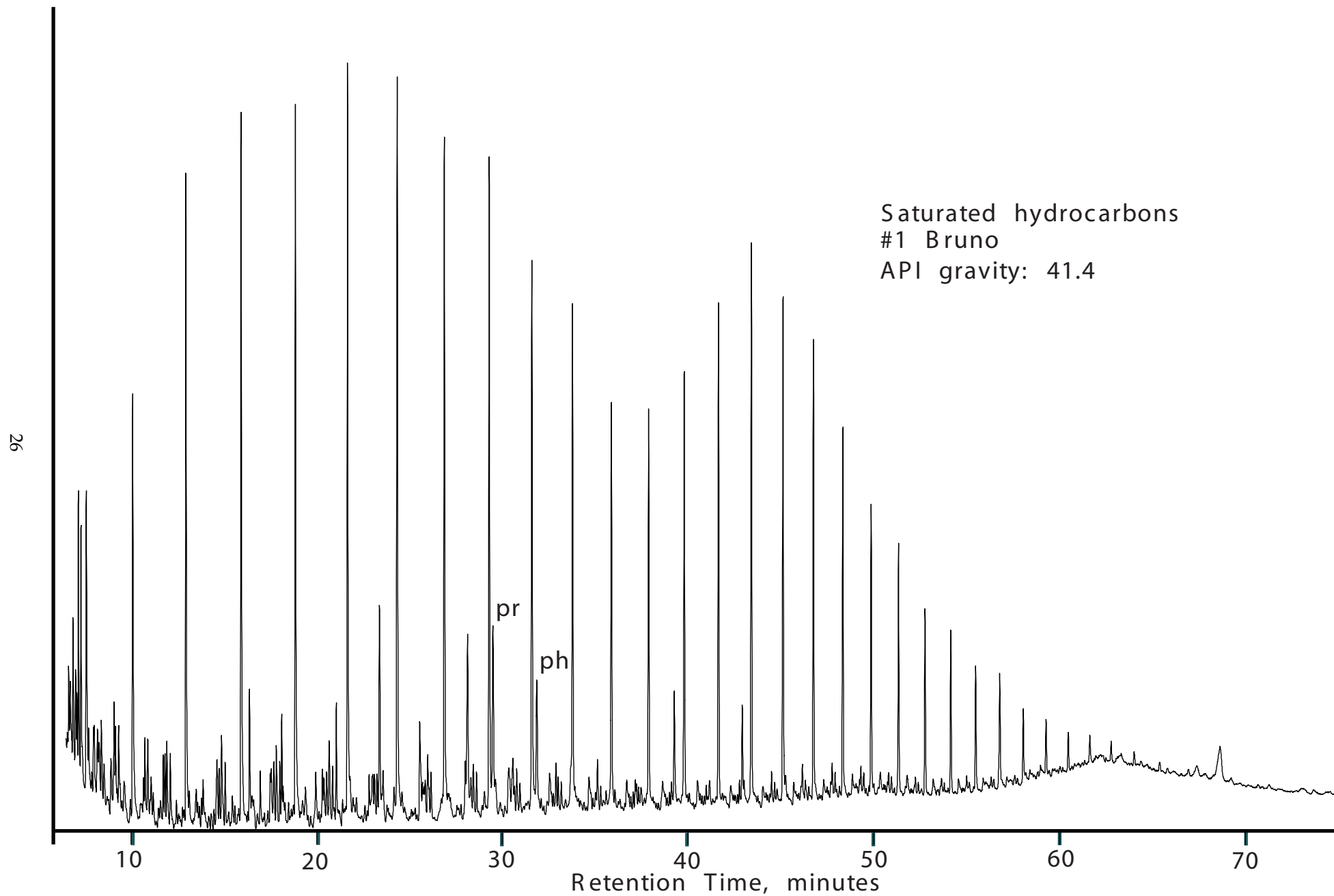


Figure 6B: Saturated hydrocarbon fraction gas chromatogram, sample 98OH02A, #1 Bruno.

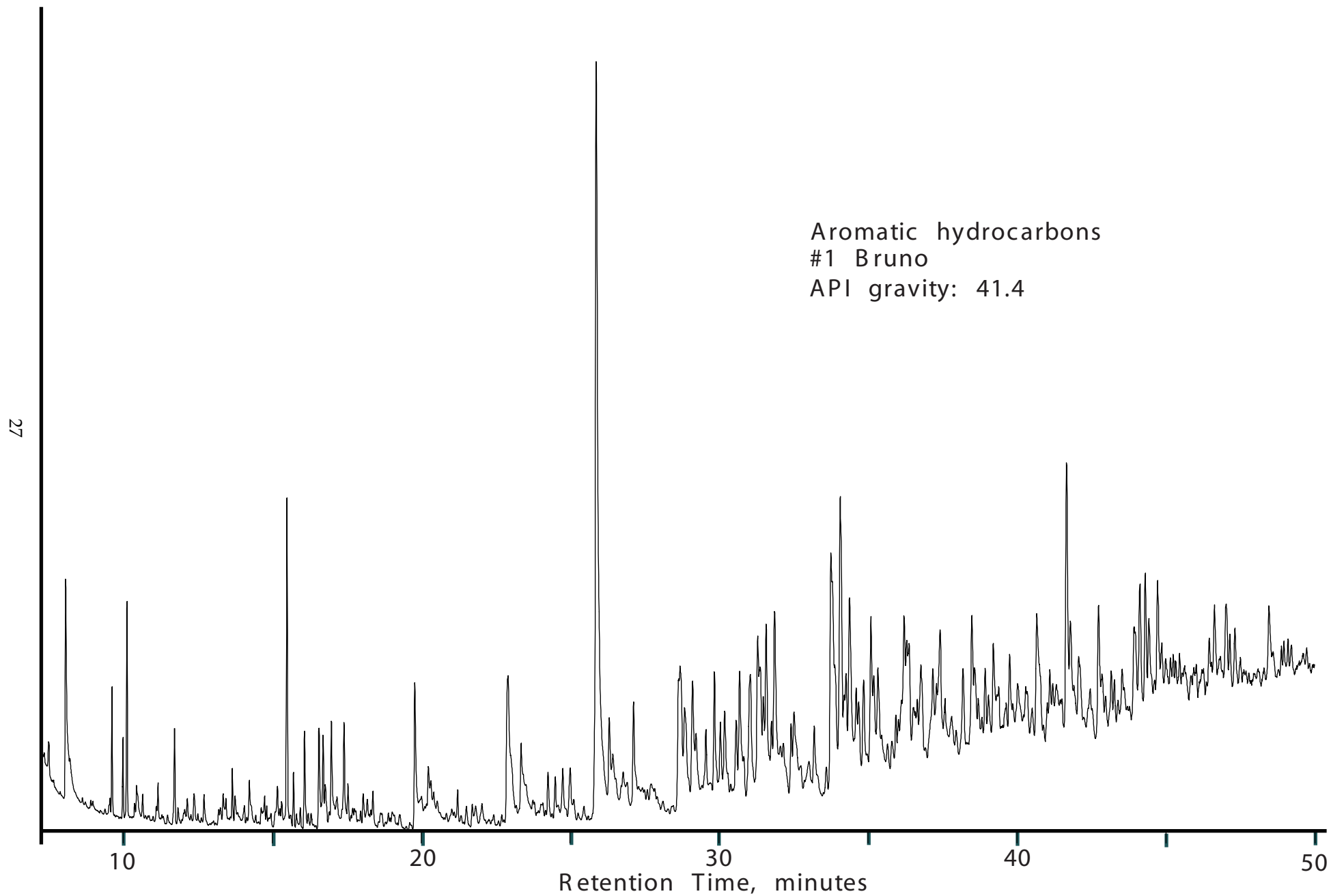


Figure 6C: Aromatic hydrocarbon fraction gas chromatogram, sample 98OH02A, #1 Bruno.

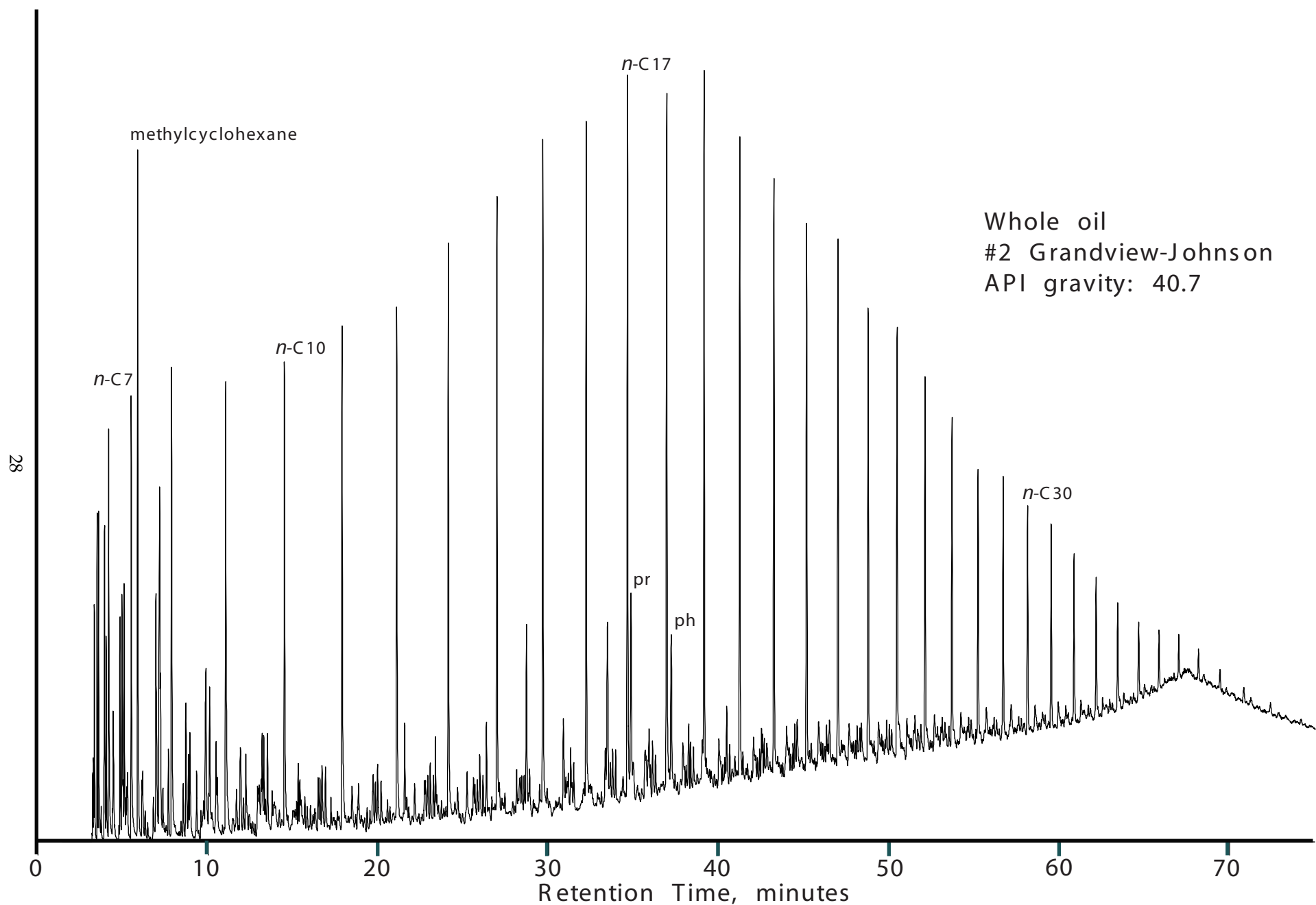


Figure 7A: Whole oil gas chromatogram, sample 98OH03A, #2 Grandview-Johnson. Selected peak identifications: *n*-CX, normal alkanes where X is the carbon number; pr, pristane; ph, phytane.

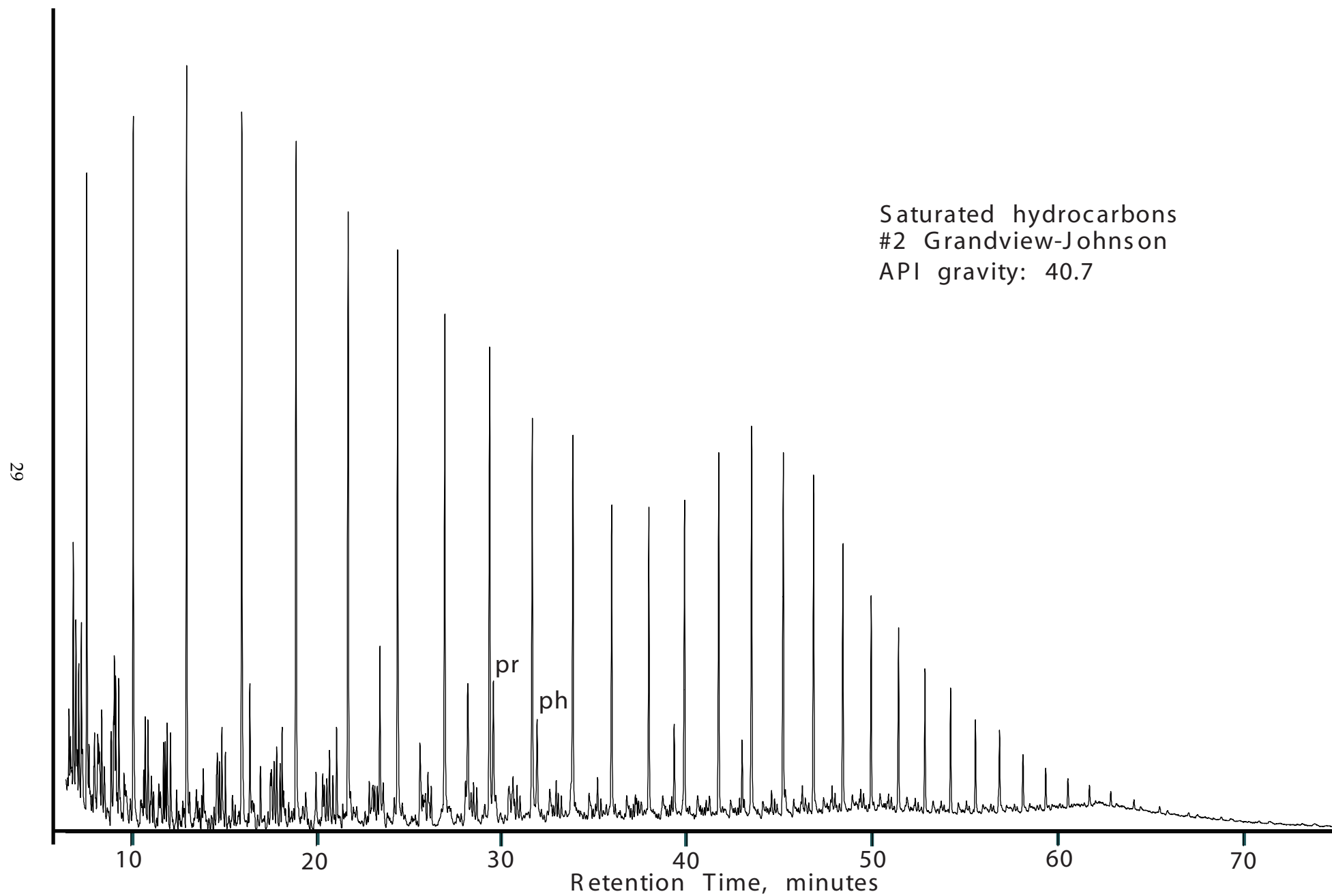


Figure 7B: Saturated hydrocarbon fraction gas chromatogram, sample 98OH03A, #2 Grandview-Johnson.

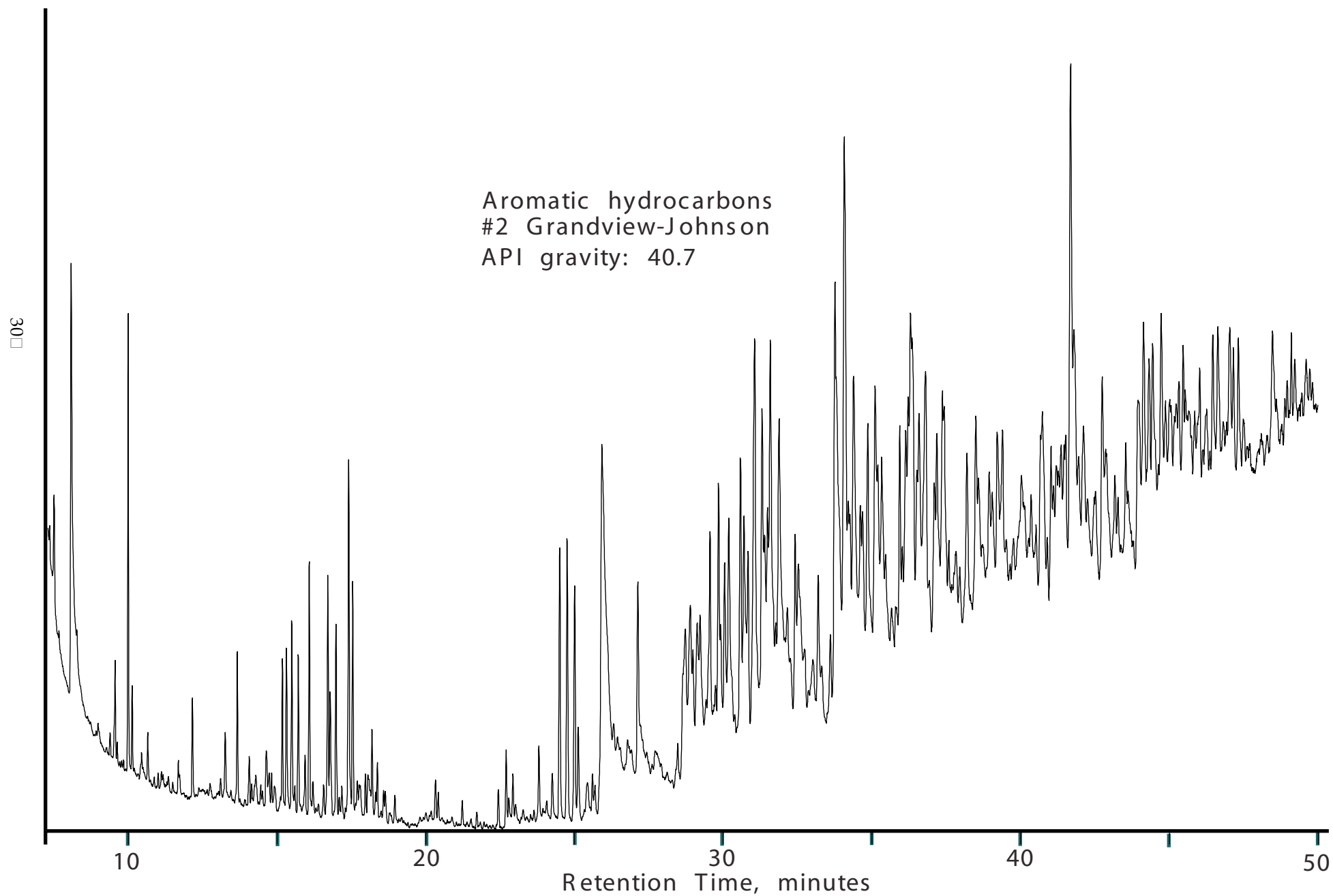


Figure 7C: Aromatic hydrocarbon fraction gas chromatogram, sample 98OH03A, #2 Grandview-Johnson.

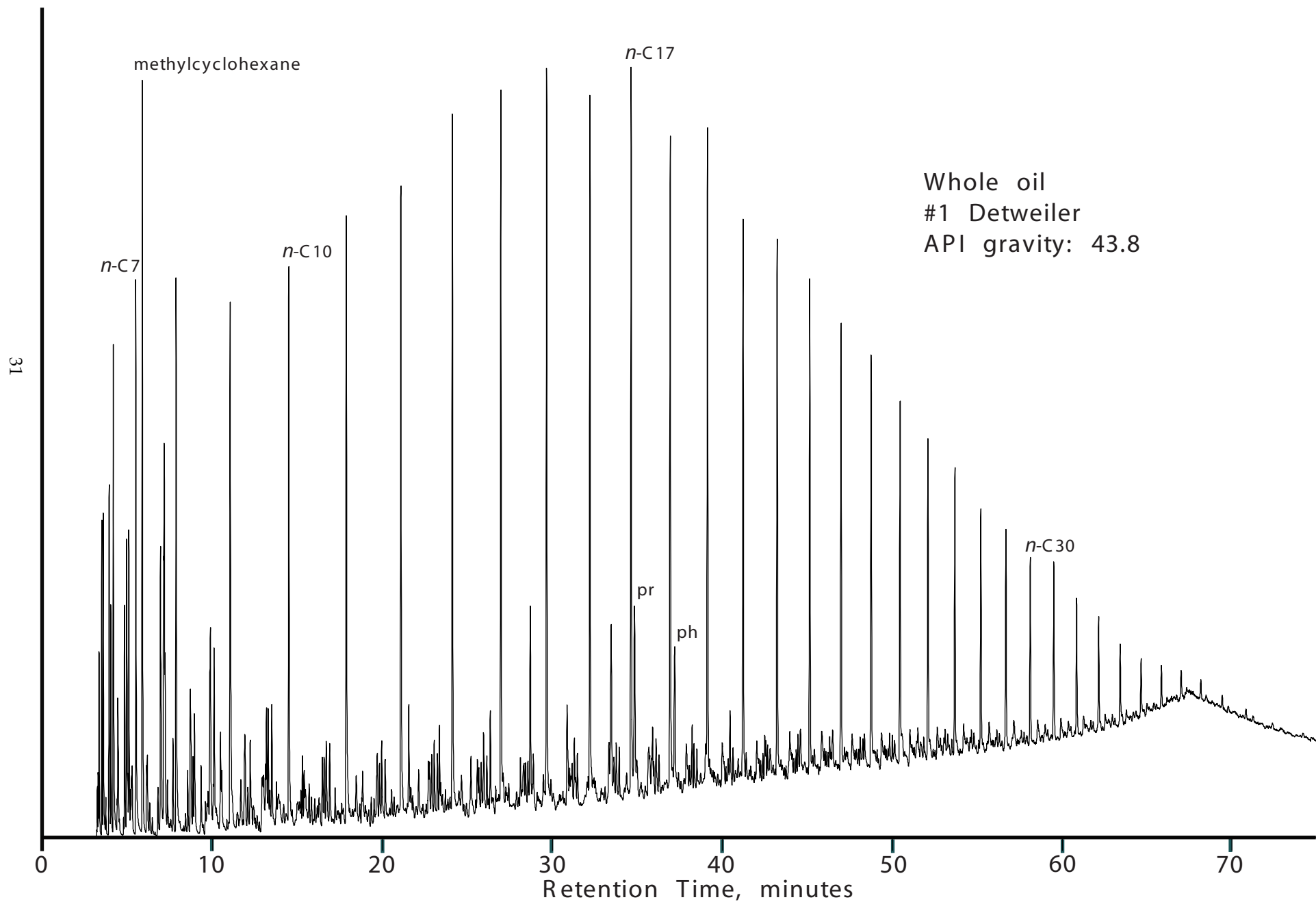


Figure 8A: Whole oil gas chromatogram, sample 98OH04A, #1 Detweiler. Selected peak identifications: *n*-CX, normal alkanes where X is the carbon number; pr, pristane; ph, phytane.

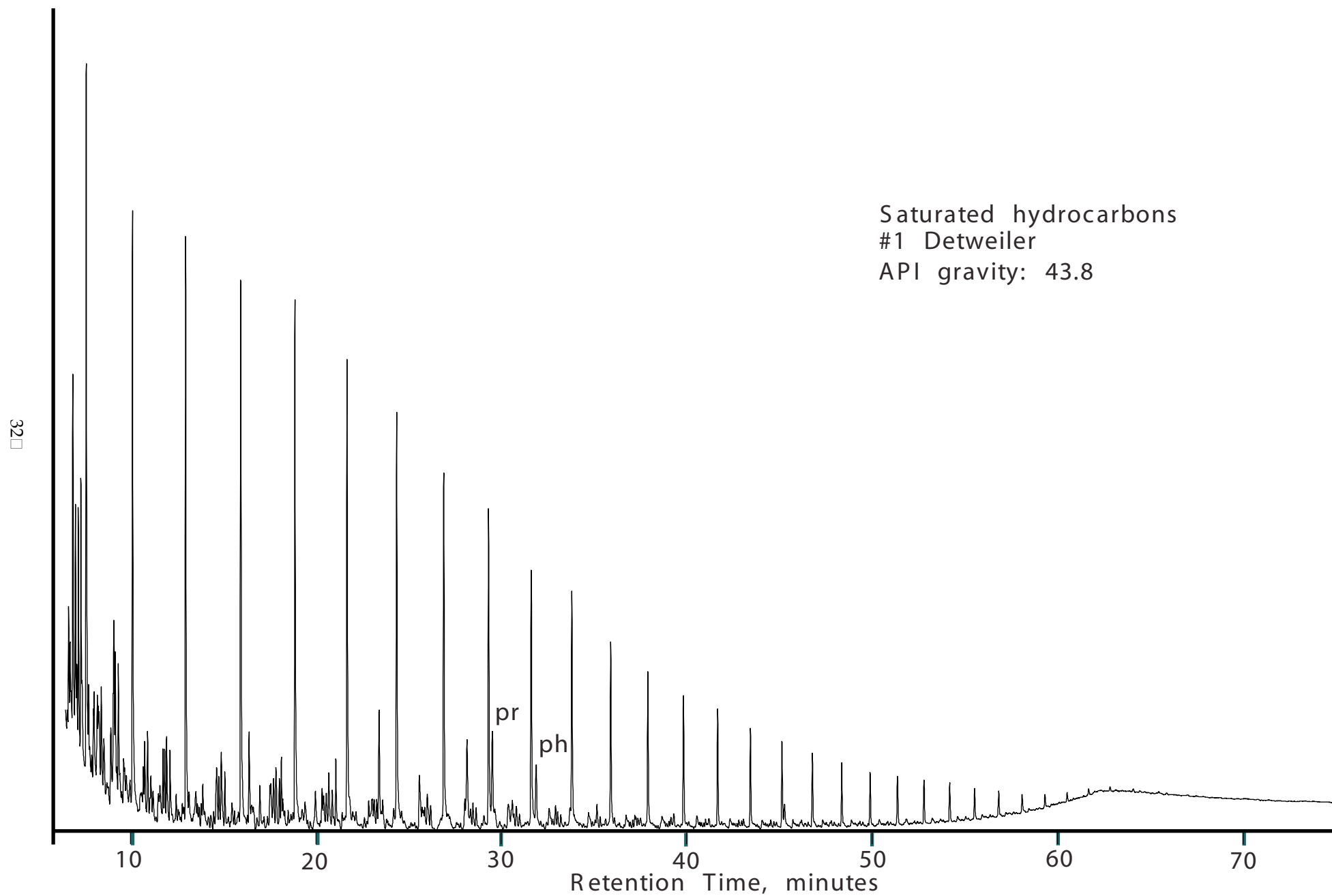


Figure 8B: Saturated hydrocarbon fraction gas chromatogram, sample 98OH04A, #1 Detweiler.

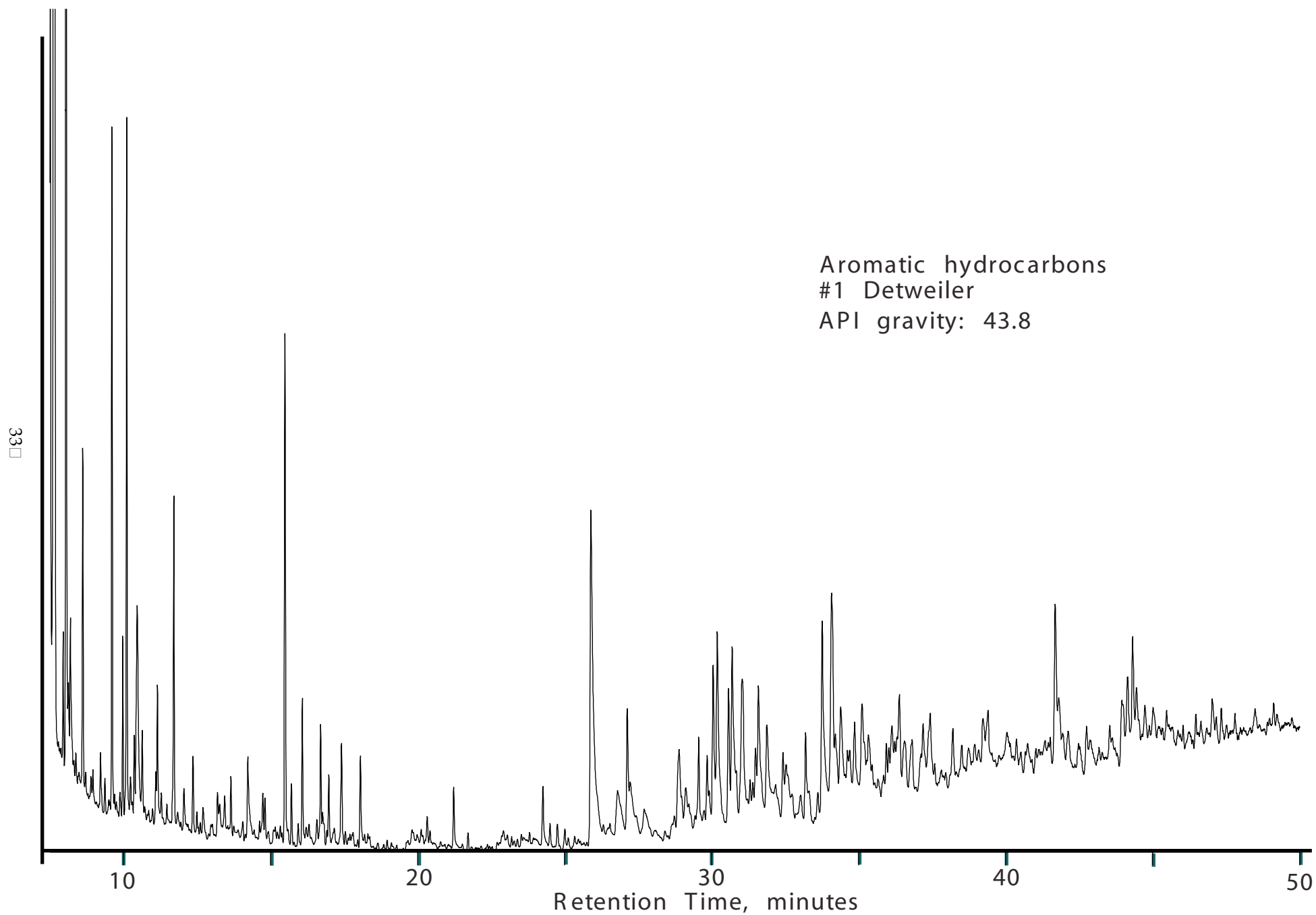


Figure 8C: Aromatic hydrocarbon fraction gas chromatogram, sample 98OH04A, #1 Detweiler.

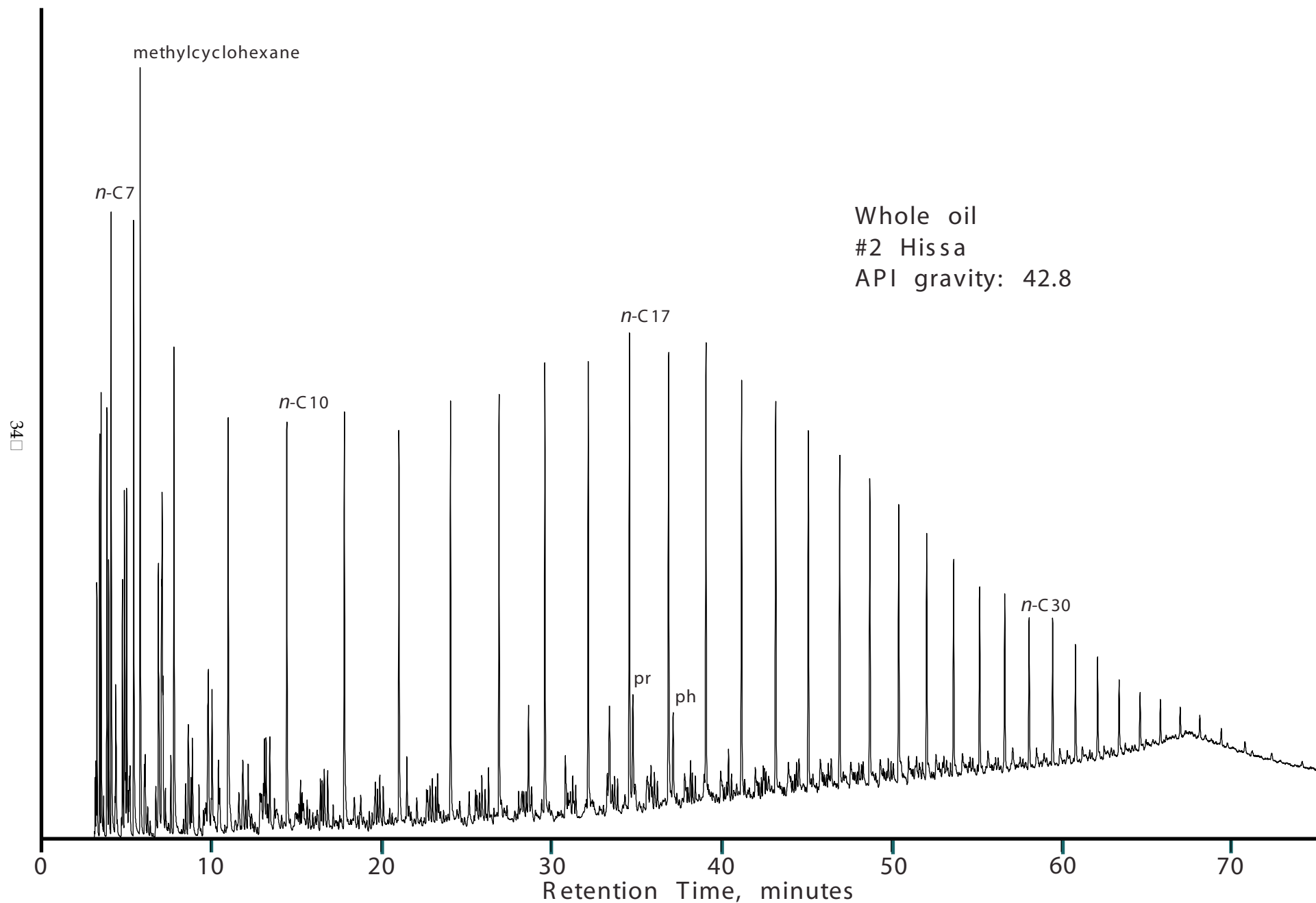


Figure 9A: Whole oil gas chromatogram, sample 98OH05A, #2 Hissa, collected from a separator that also serves the #1 Hissa well. Selected peak identifications: *n*-CX, normal alkanes where X is the carbon number; pr, pristane; ph, phytane.

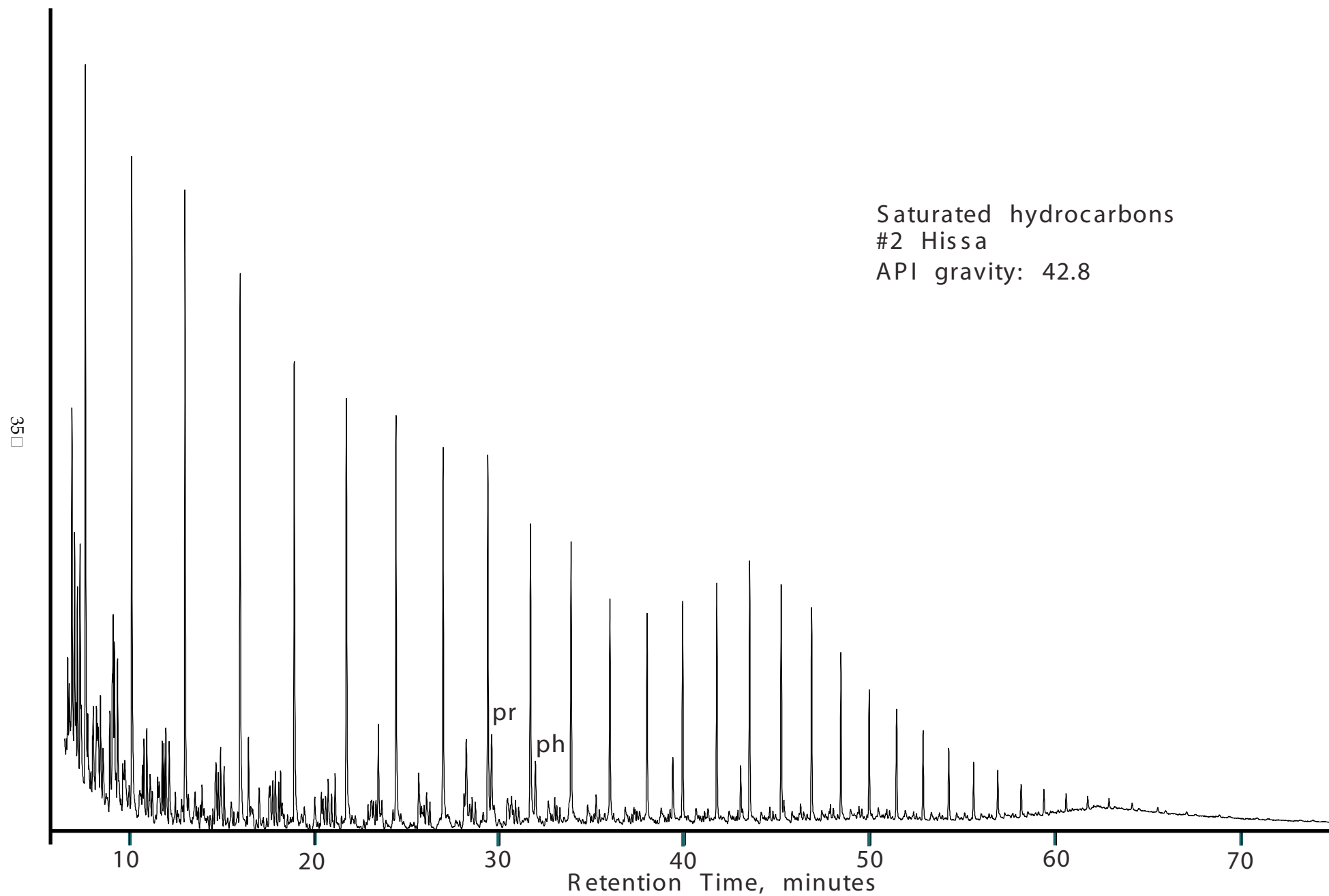


Figure 9B: Saturated hydrocarbon fraction gas chromatogram, sample 98OH05A, #2 Hissa, collected from a separator that also serves the #1 Hissa well..

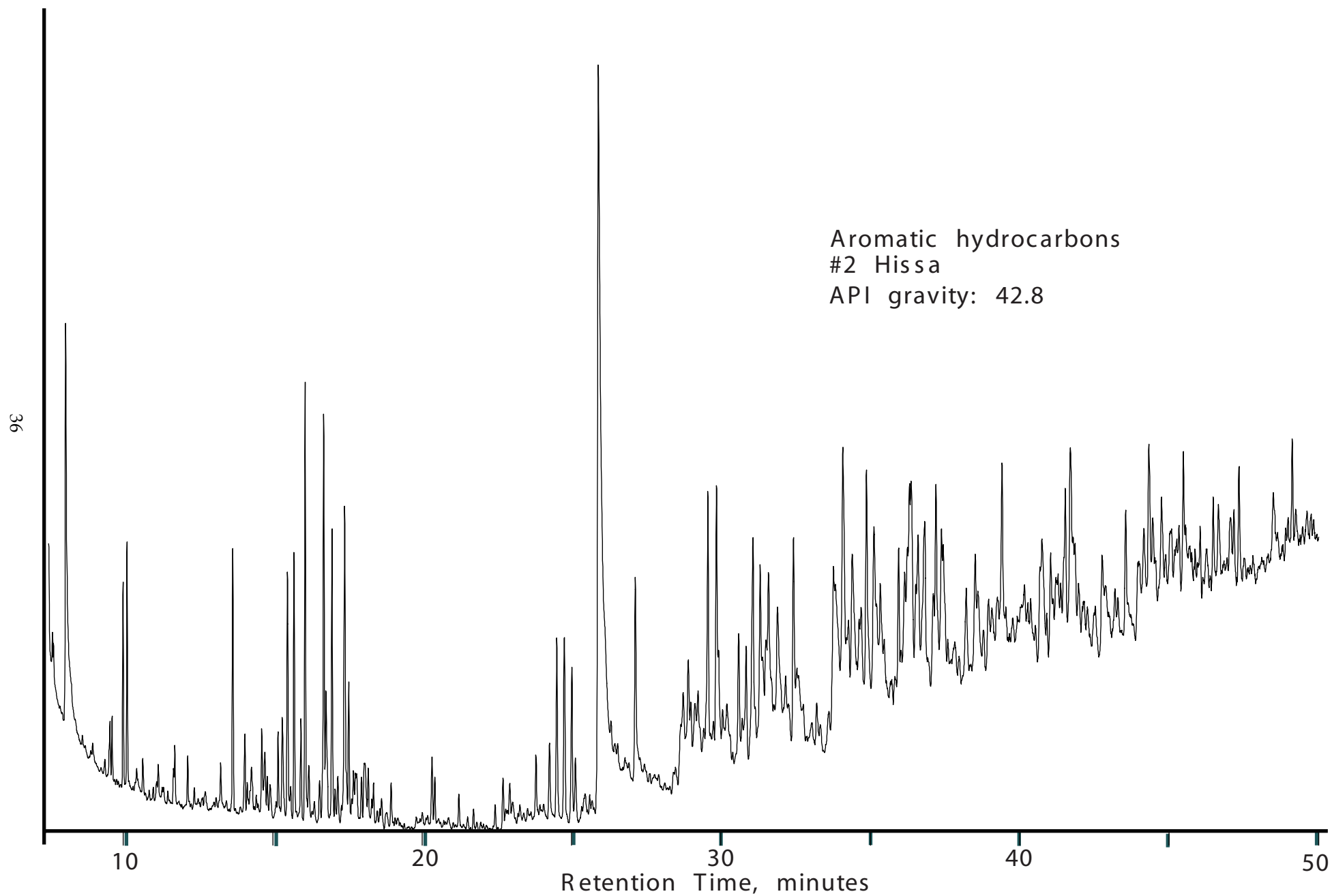


Figure 9C: Aromatic hydrocarbon fraction gas chromatogram, sample 98OH05A, #2 Hissa, collected from a separator that also serves the #1 Hissa well.

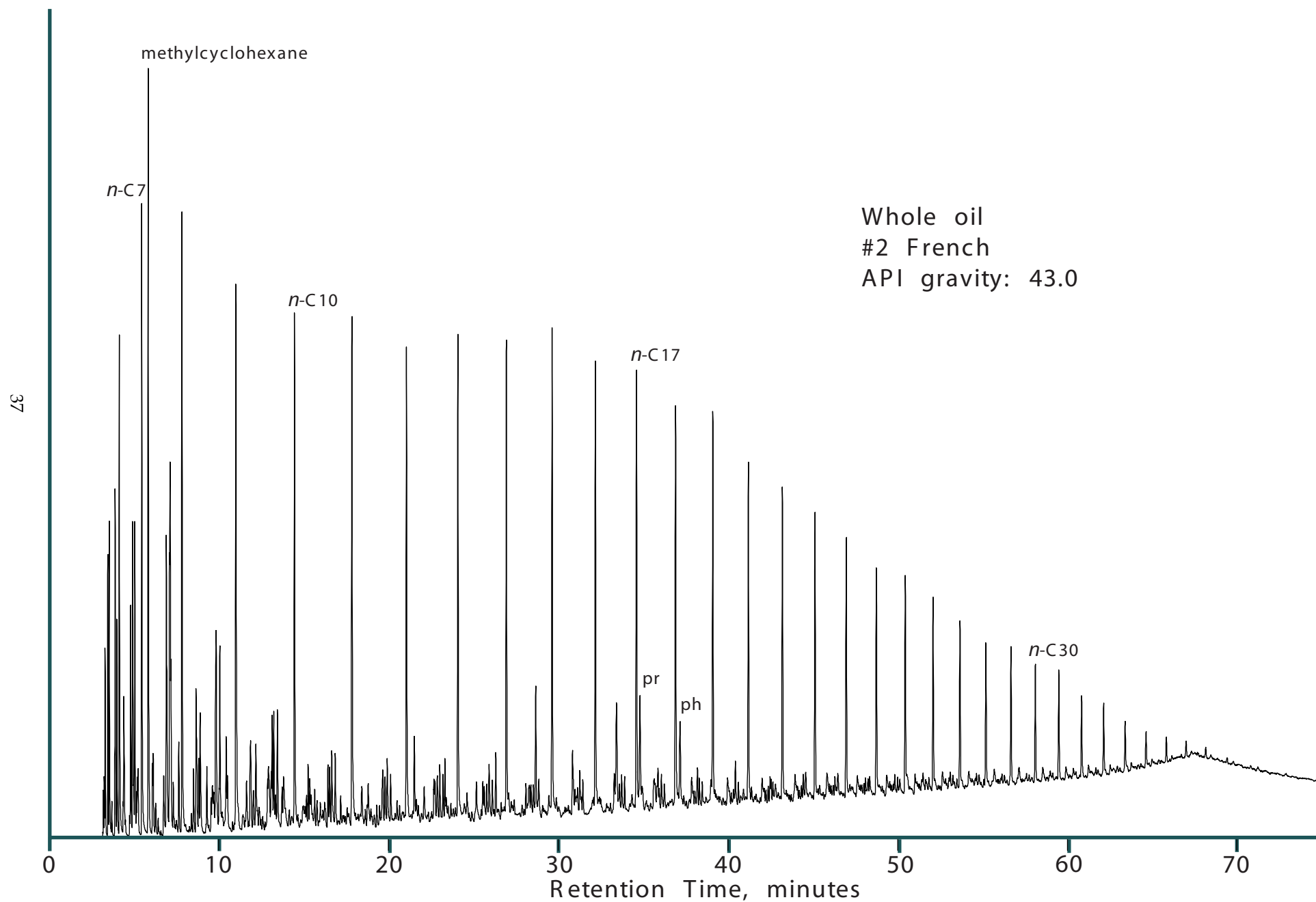


Figure 10A: Whole oil gas chromatogram, sample 98OH06A, #2 French. Selected peak identifications: *n*-CX, normal alkanes where X is the carbon number; pr, pristane; ph, phytane.

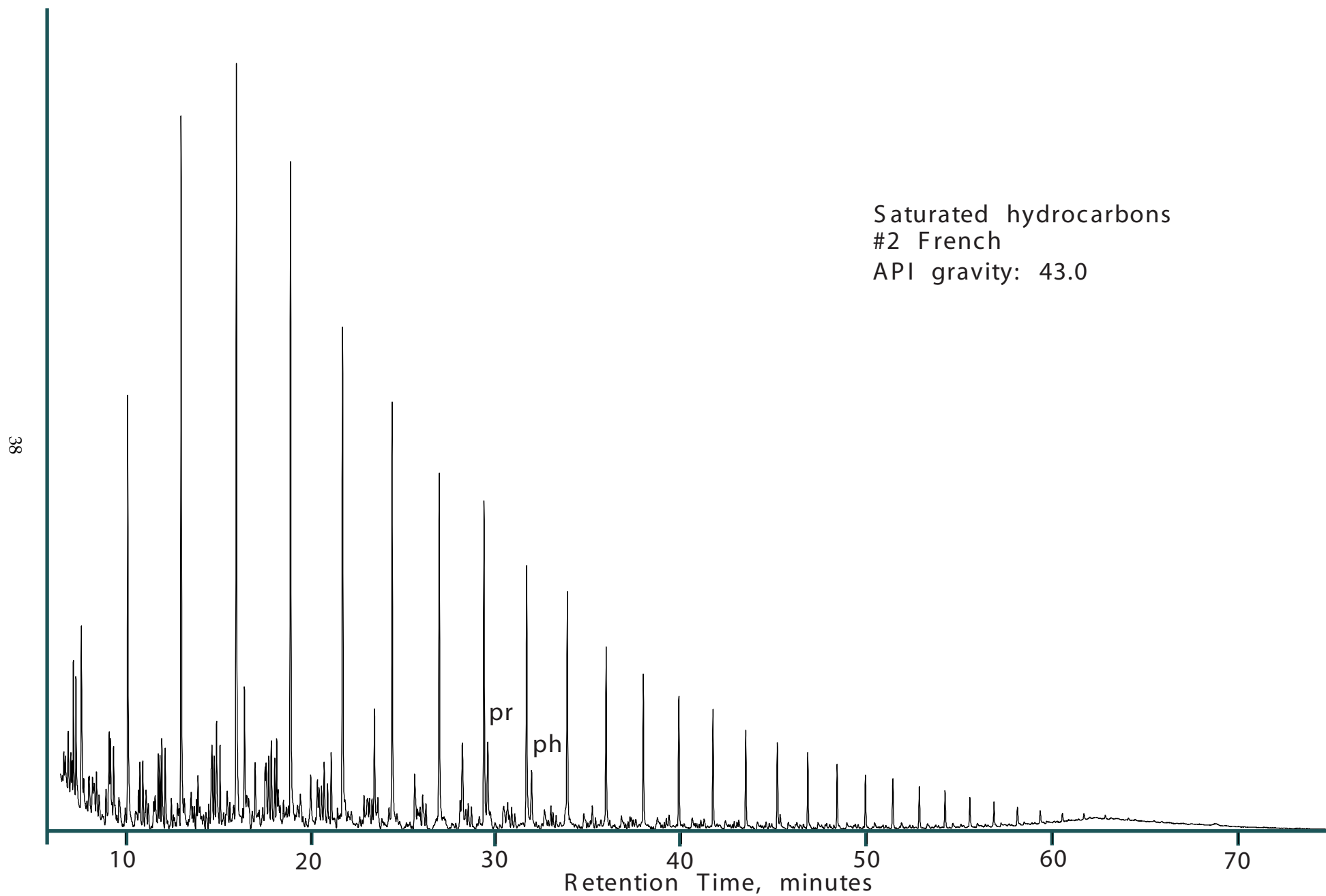


Figure 10B: Saturated hydrocarbon fraction gas chromatogram, sample 98OH06A, #2 French.

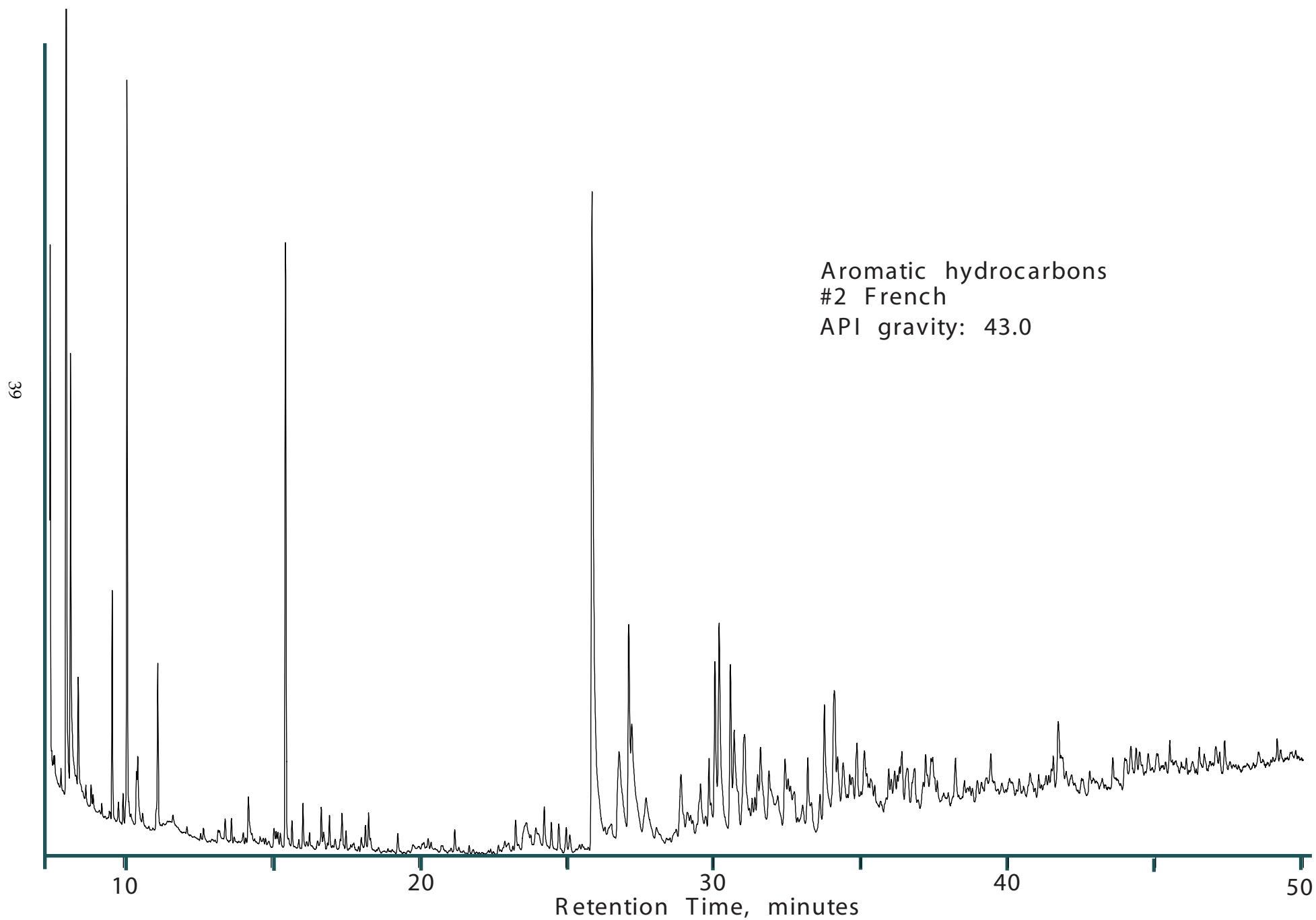


Figure 10C: Aromatic hydrocarbon fraction gas chromatogram, sample 98OH06A, #2 French.

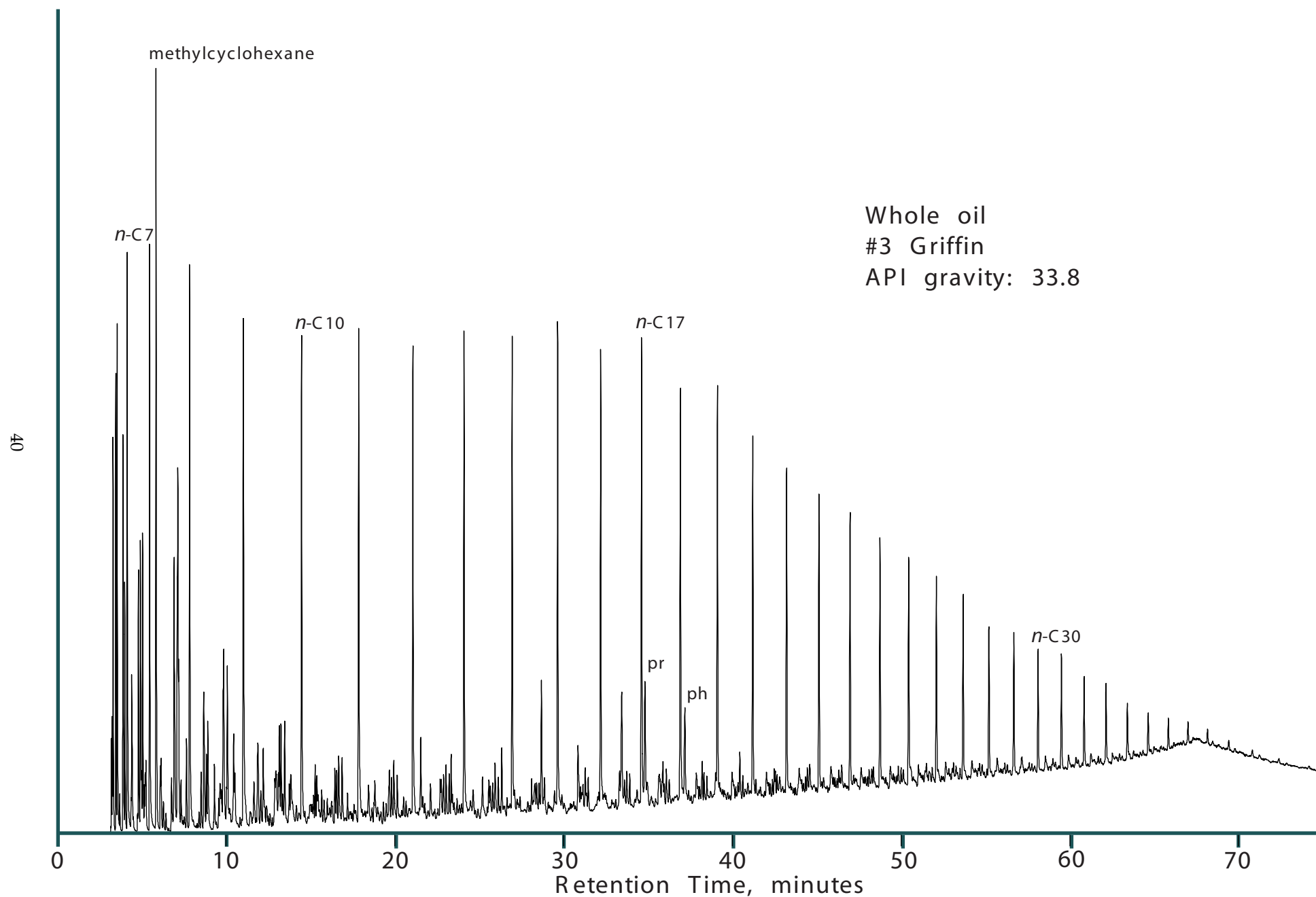


Figure 11A: Whole oil gas chromatogram, sample 98OH07A, #3 Griffin. Selected peak identifications: *n*-CX, normal alkanes where X is the carbon number; pr, pristane; ph, phytane.

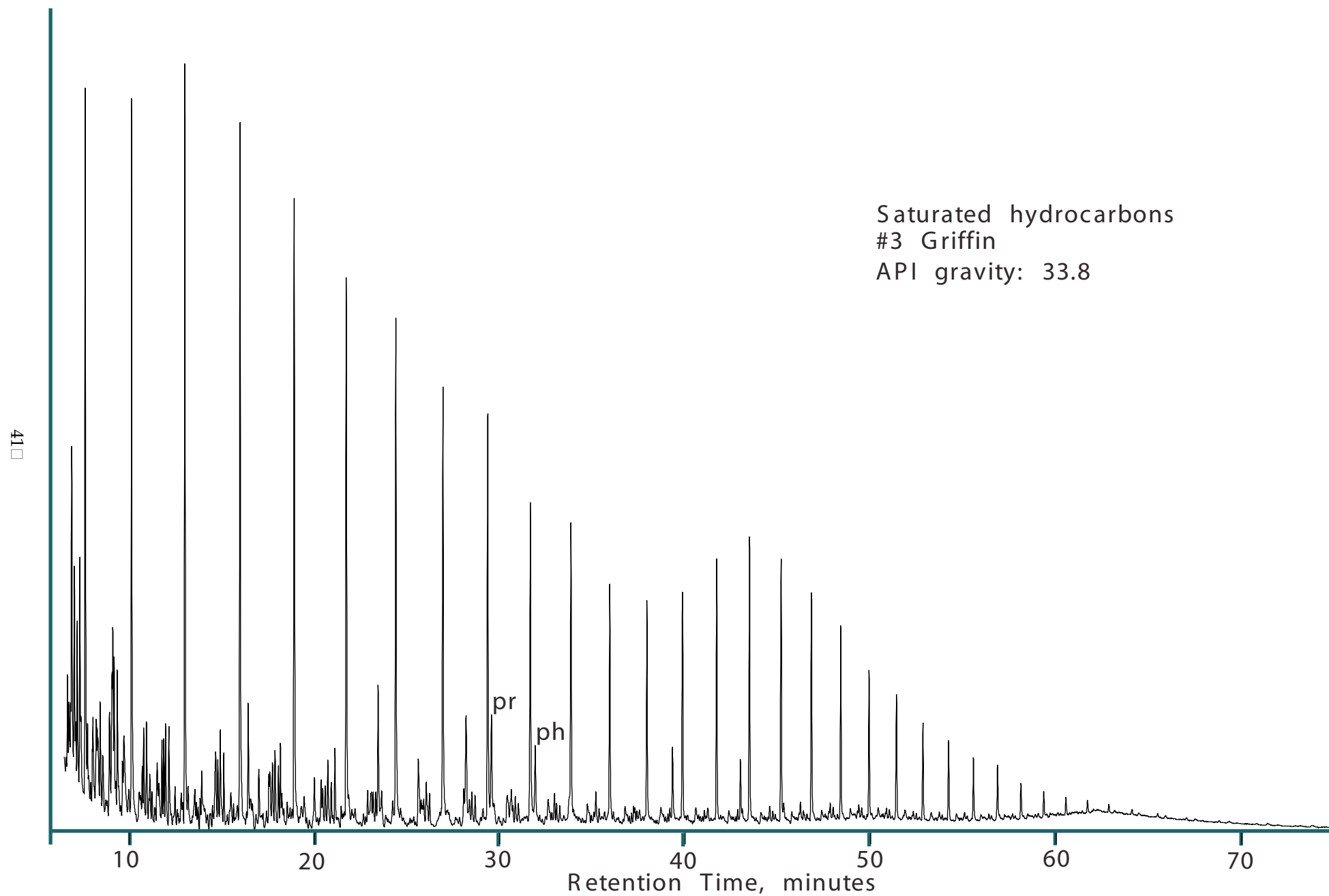


Figure 11B: Saturated hydrocarbon fraction gas chromatogram, sample 98OH07A, #3 Griffin.

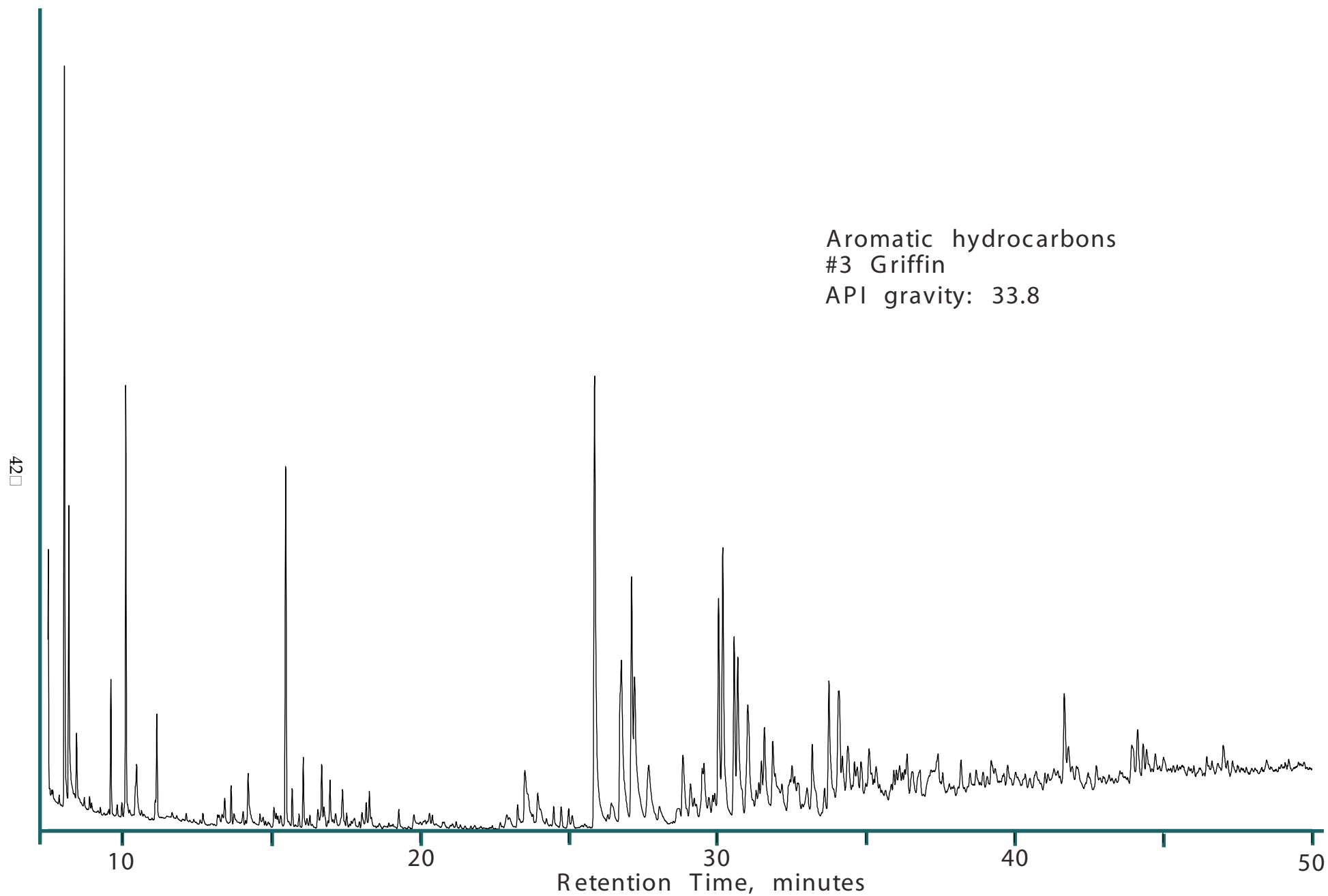


Figure 11C: Aromatic hydrocarbon fraction gas chromatogram, sample 98OH07A, #3 Griffin.

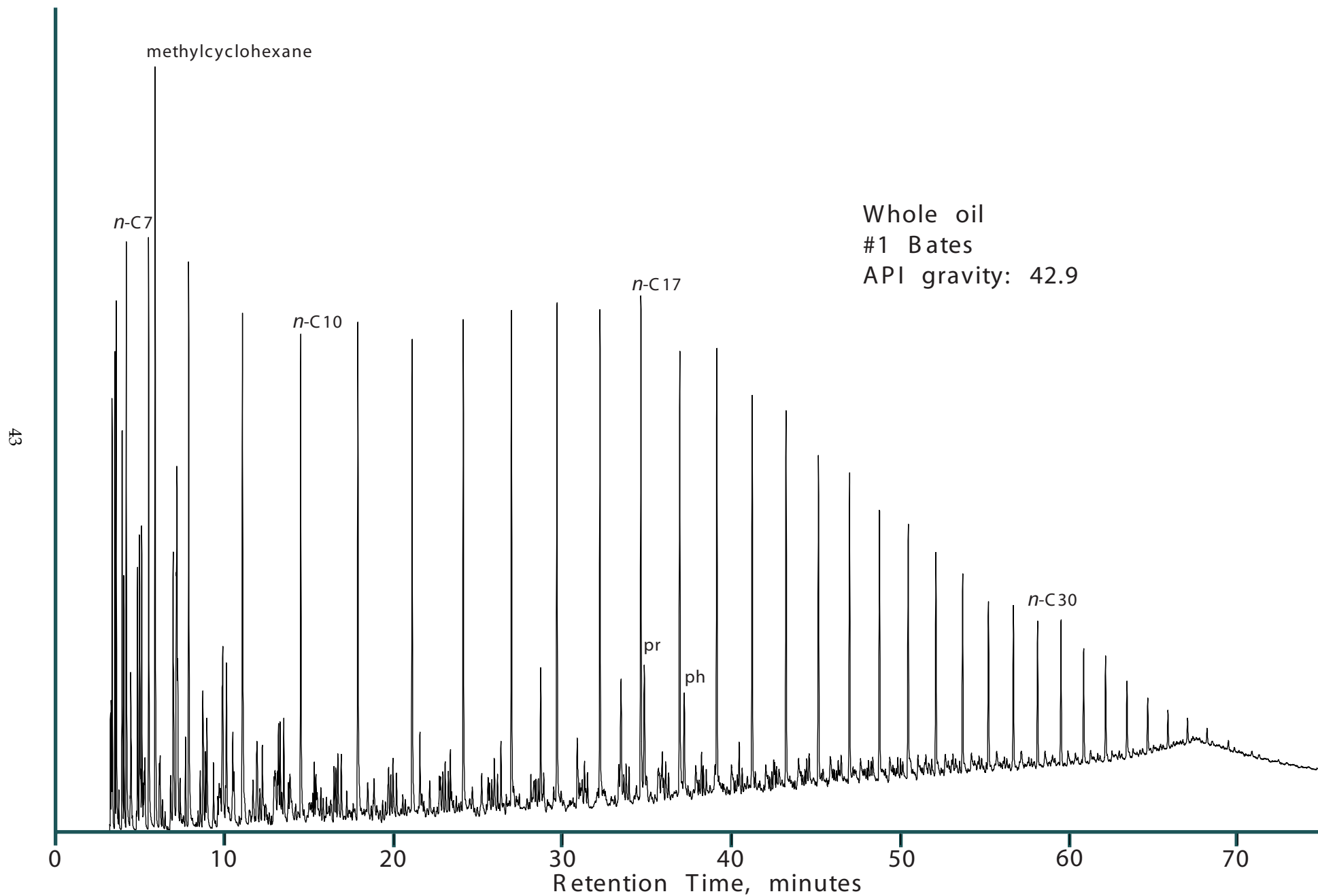


Figure 12A: Whole oil gas chromatogram, sample 98OH08, #1 Bates. Selected peak identifications: *n*-CX, normal alkanes where X is the carbon number; pr, pristane; ph, phytane.

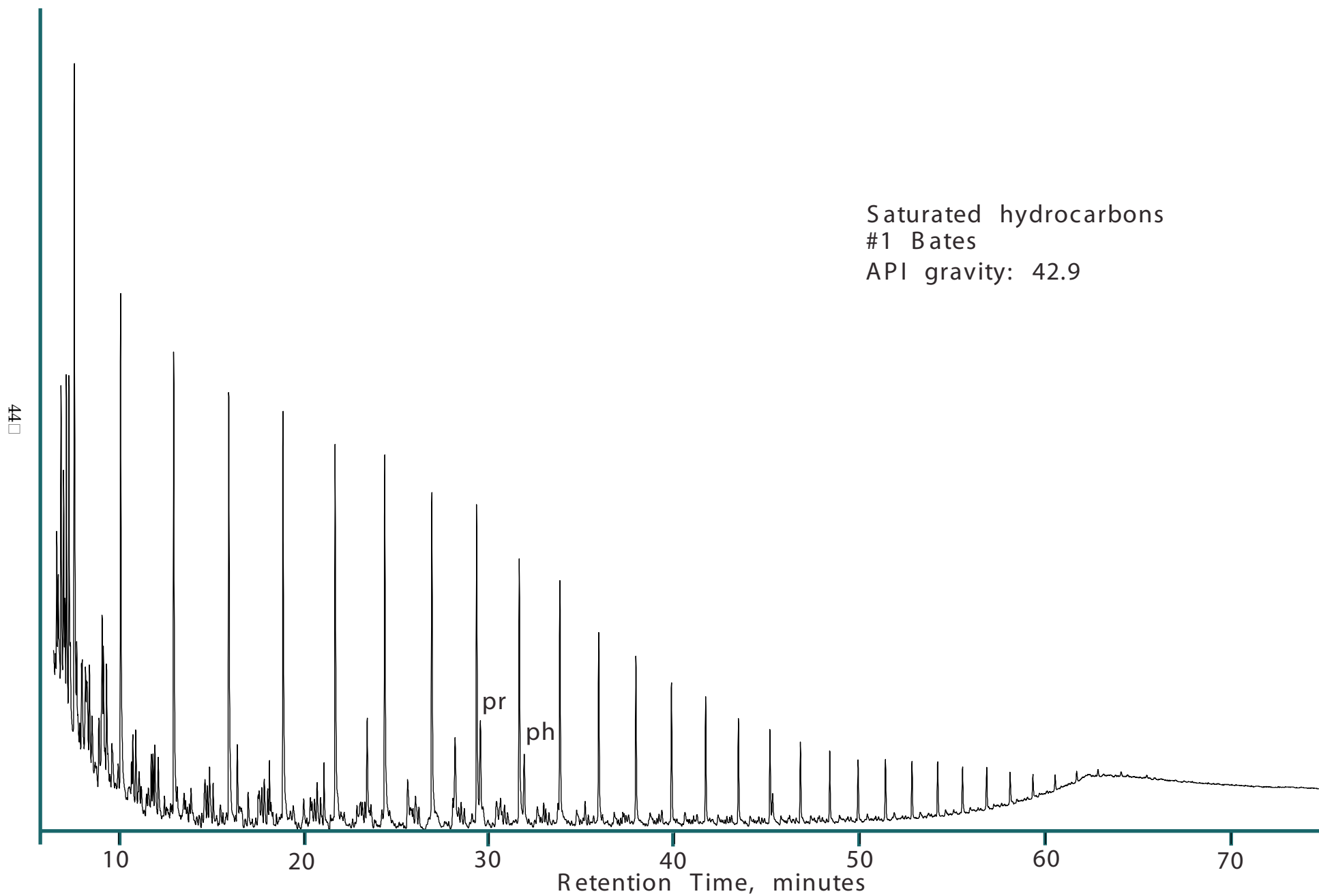


Figure 12B: Saturated hydrocarbon fraction gas chromatogram, sample 98OH08, #1Bates.

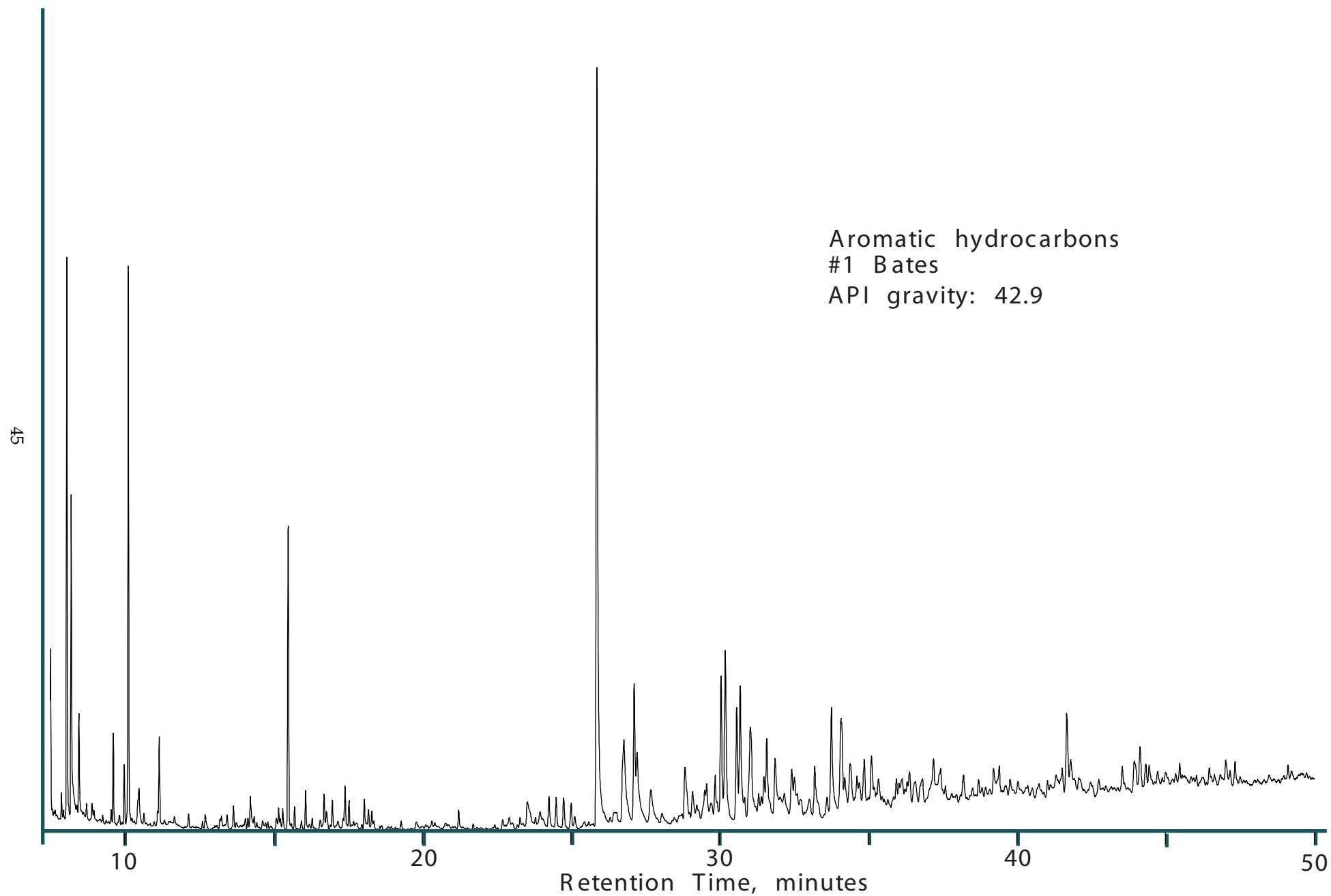


Figure 12C: Aromatic hydrocarbon fraction gas chromatogram, sample 98OH08, #1 Bates.

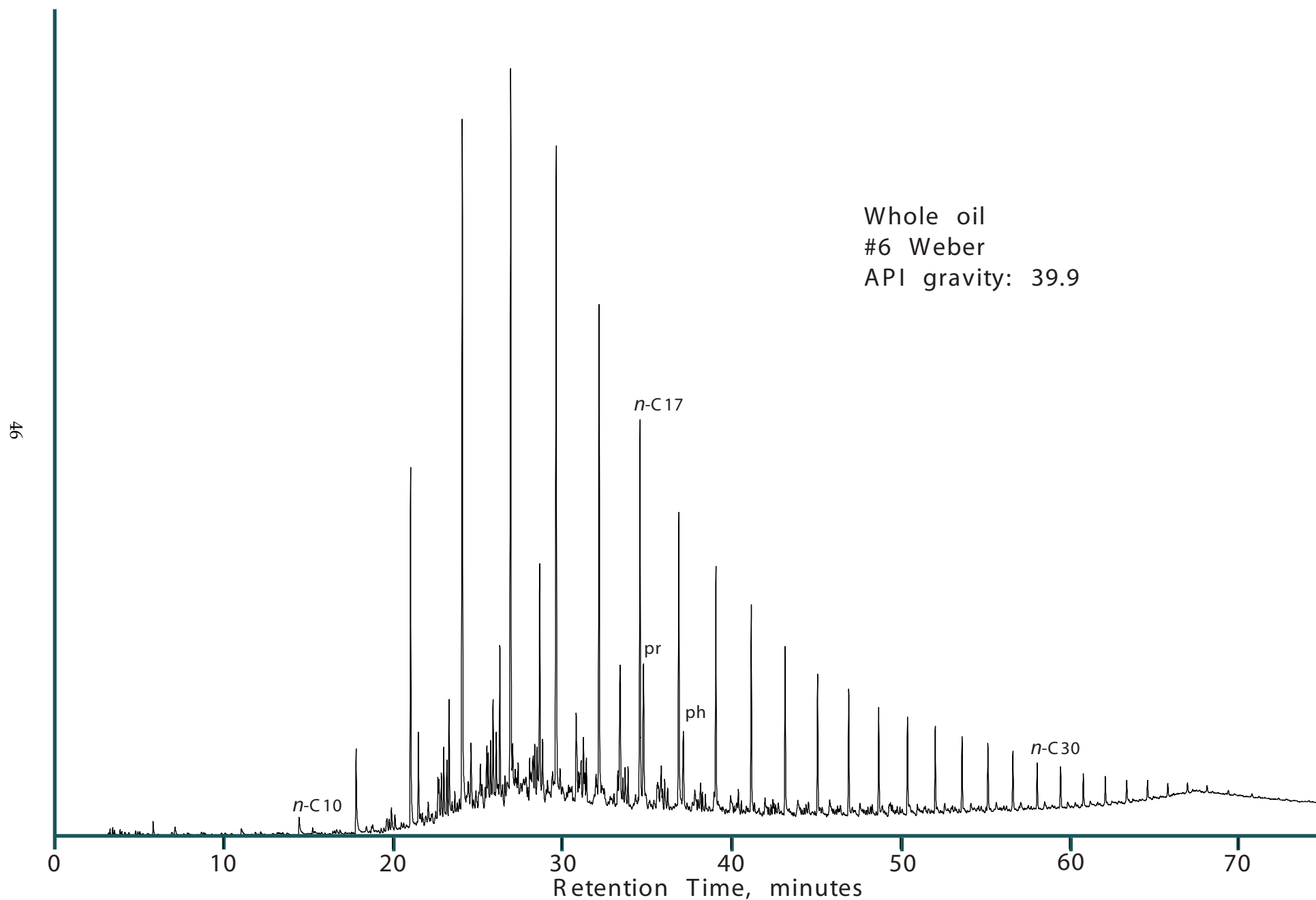


Figure 13A: Whole oil gas chromatogram, sample 98PA02, #6 Weber. Selected peak identifications: *n*-CX, normal alkanes where X is the carbon number; pr, pristane; ph, phytane.

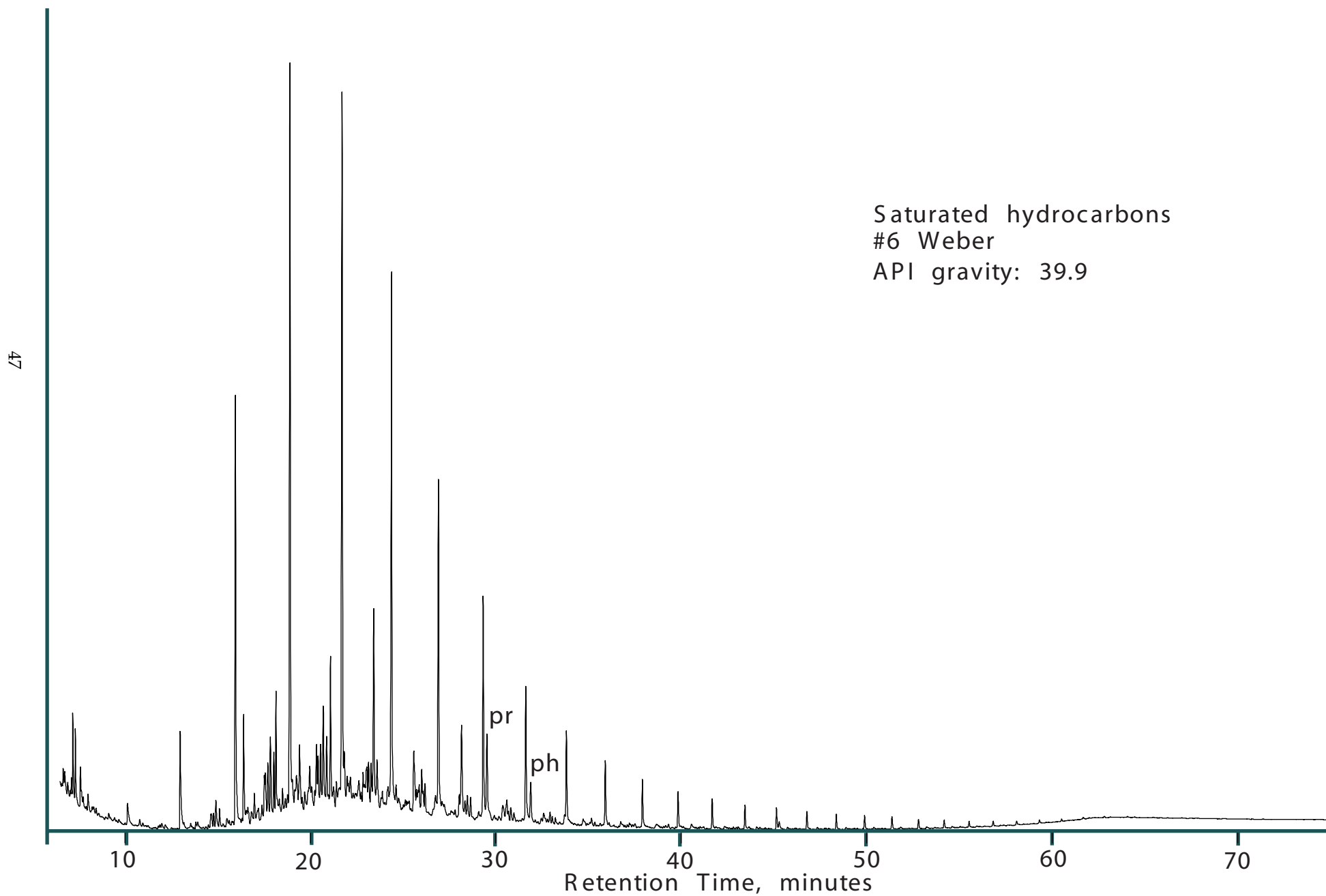


Figure 13B: Saturated hydrocarbon fraction gas chromatogram, sample 98PA02, #6 Weber.

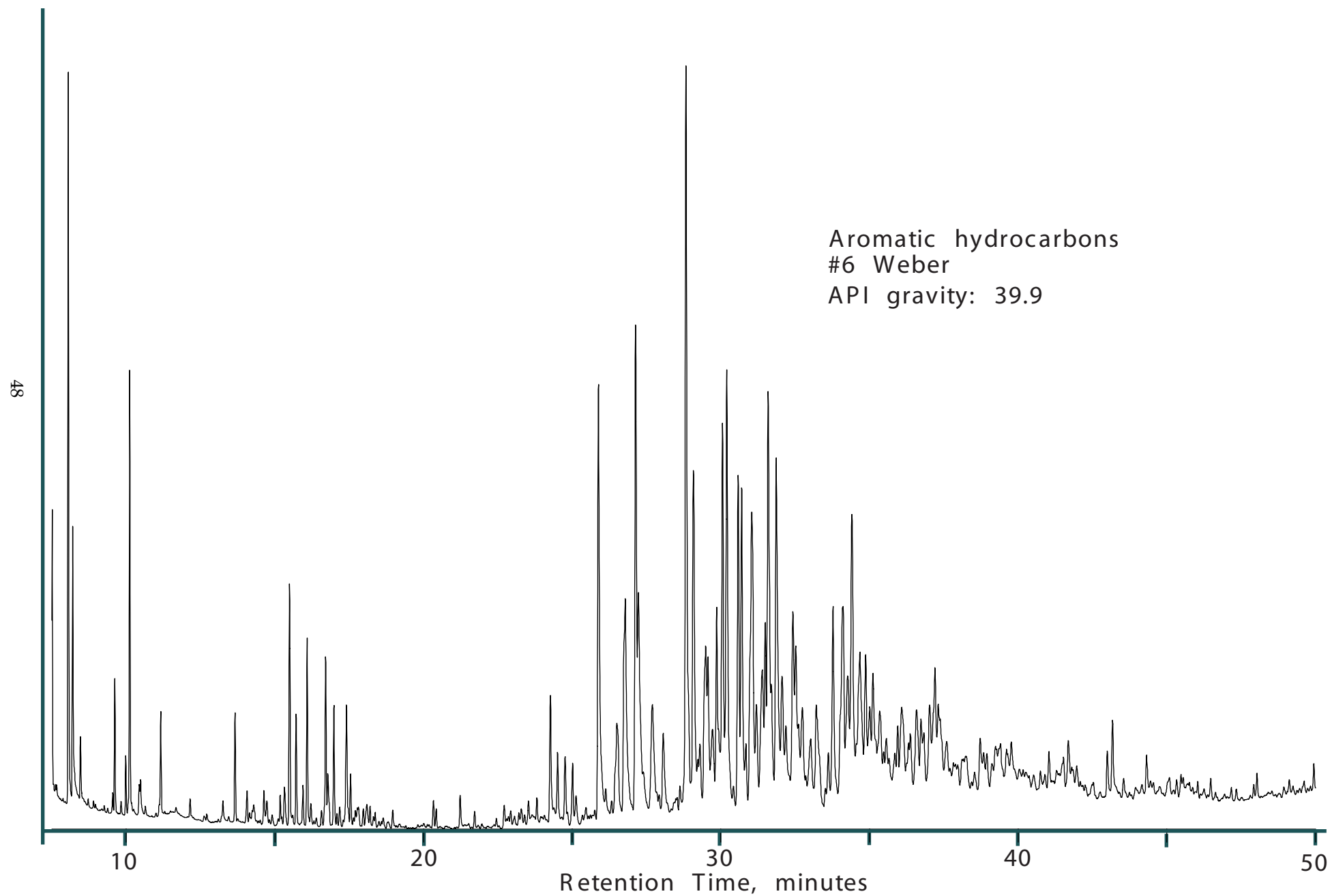


Figure 13C: Aromatic hydrocarbon fraction gas chromatogram, sample 98PA02, #6 Weber.

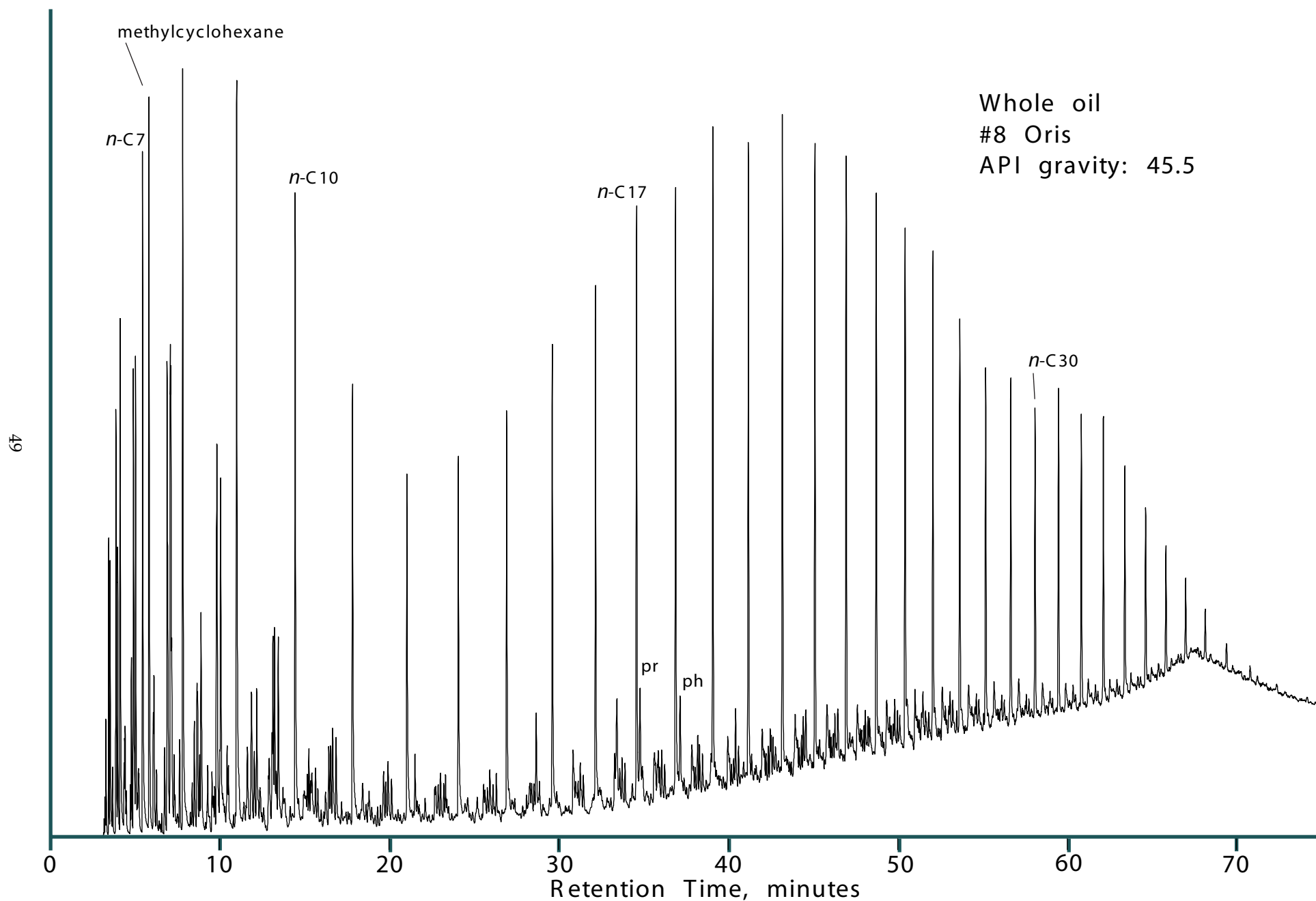


Figure 14A: Whole oil gas chromatogram, sample 98PA05A, #8 Oris. Selected peak identifications: *n*-CX, normal alkanes where X is the carbon number; pr, pristane; ph, phytane.

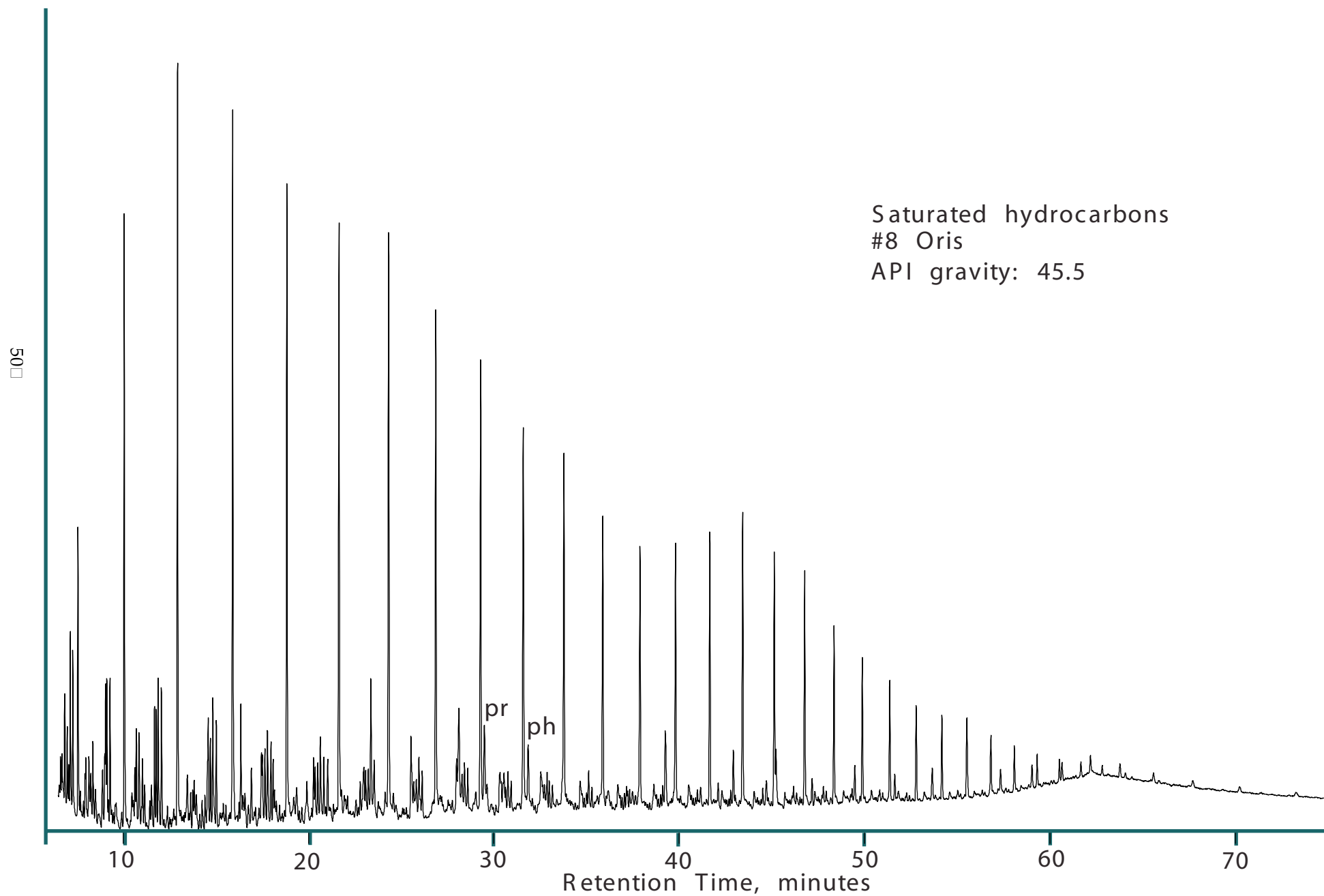


Figure 14B: Saturated hydrocarbon fraction gas chromatogram, sample 98PA05A, #8 Oris.

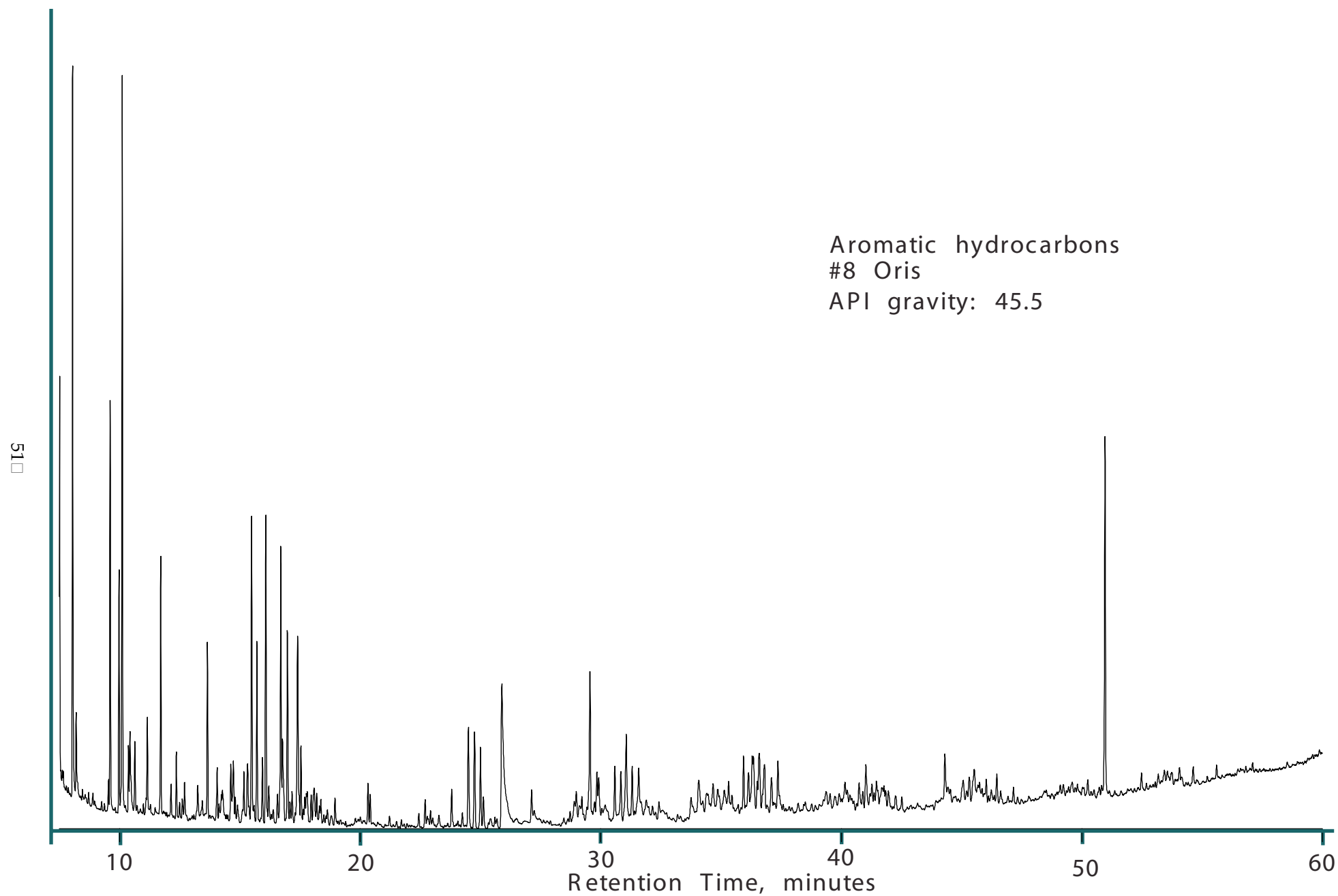


Figure 14C: Aromatic hydrocarbon fraction gas chromatogram, sample 98PA05A, #8 Oris.

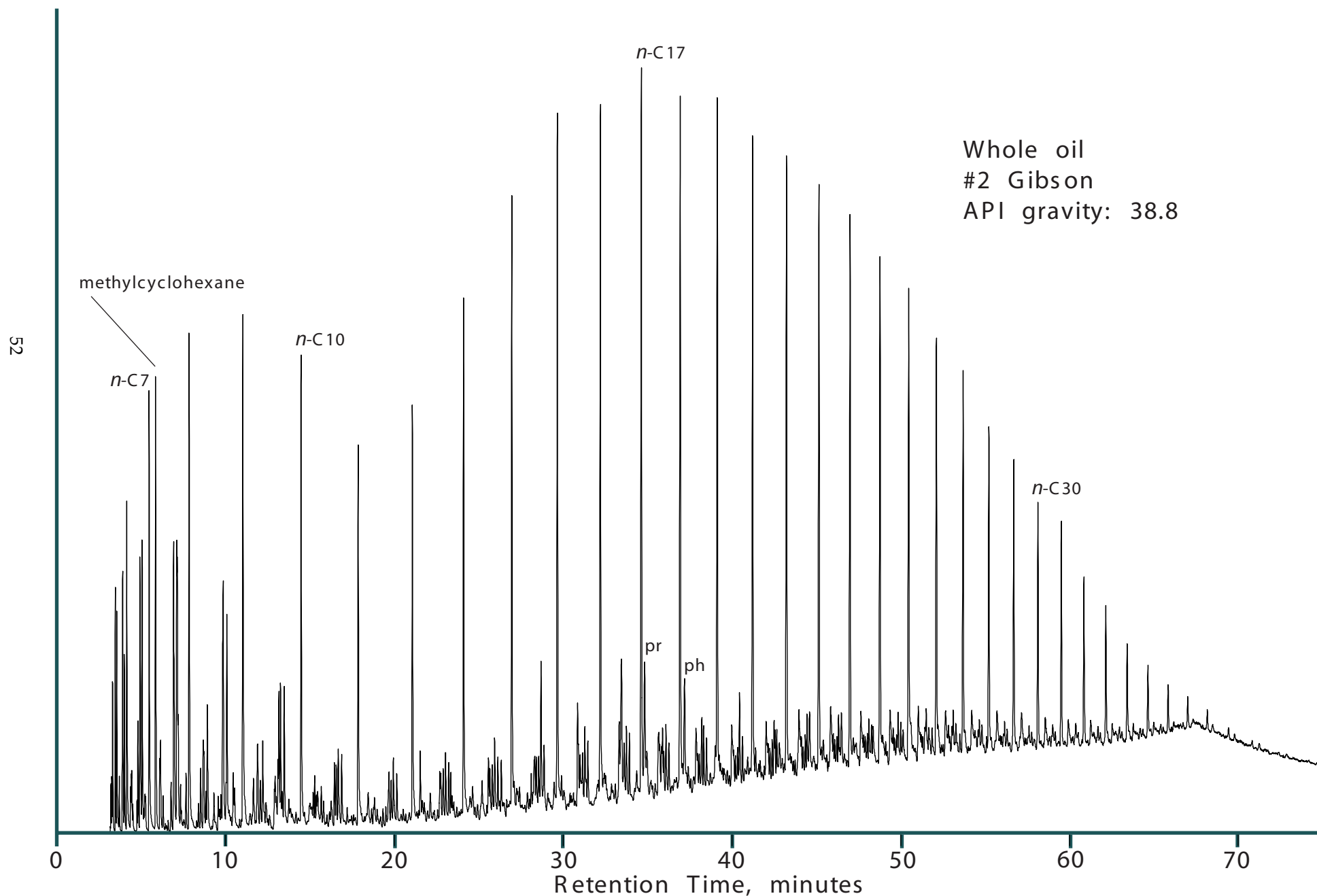


Figure 15A: Whole oil gas chromatogram, sample 98PA06A, #2 Gibson. Selected peak identifications: *n*-CX, normal alkanes where X is the carbon number; pr, pristane; ph, phytane.

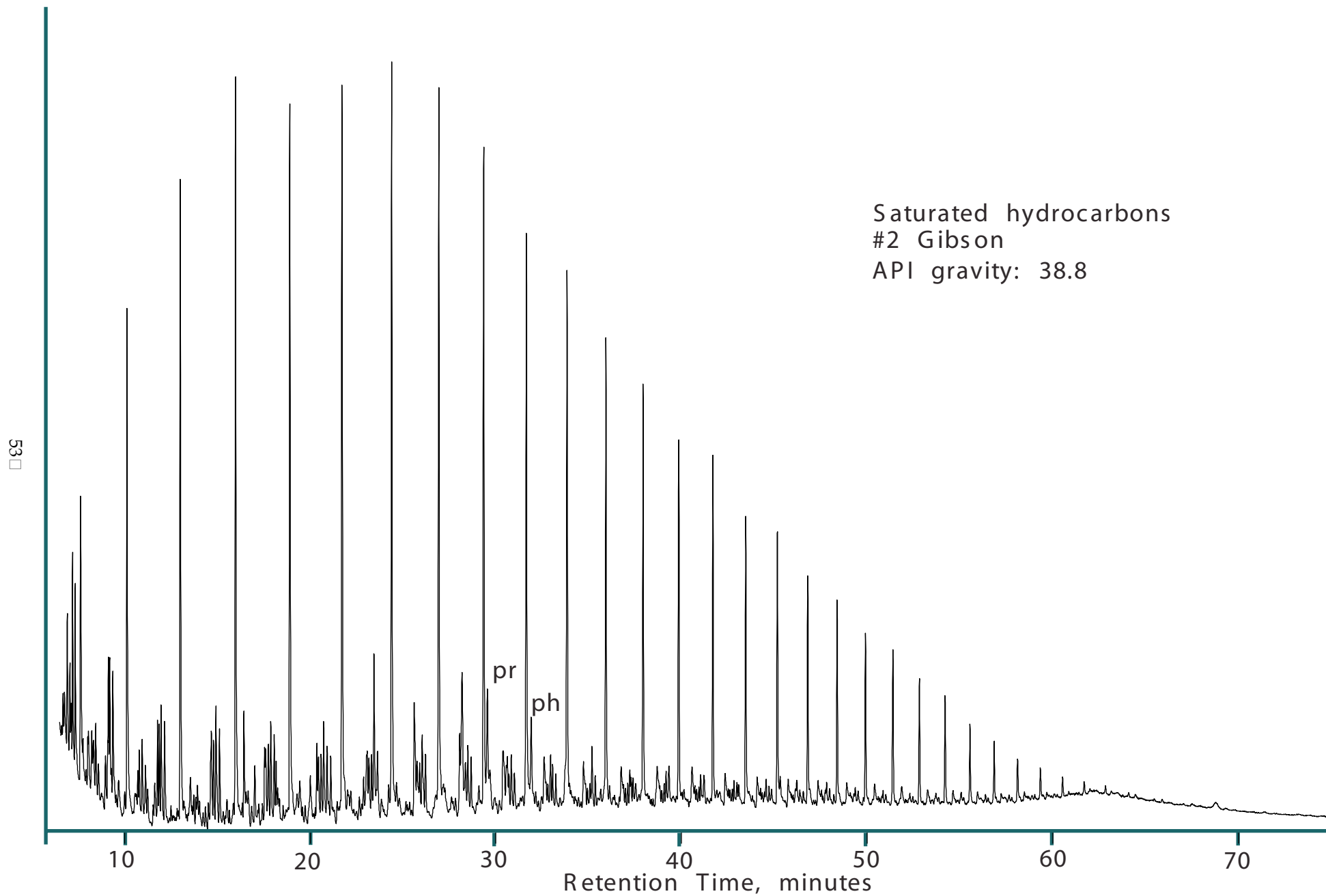


Figure 15B: Saturated hydrocarbon fraction gas chromatogram, sample 98PA06A, #2 Gibson.

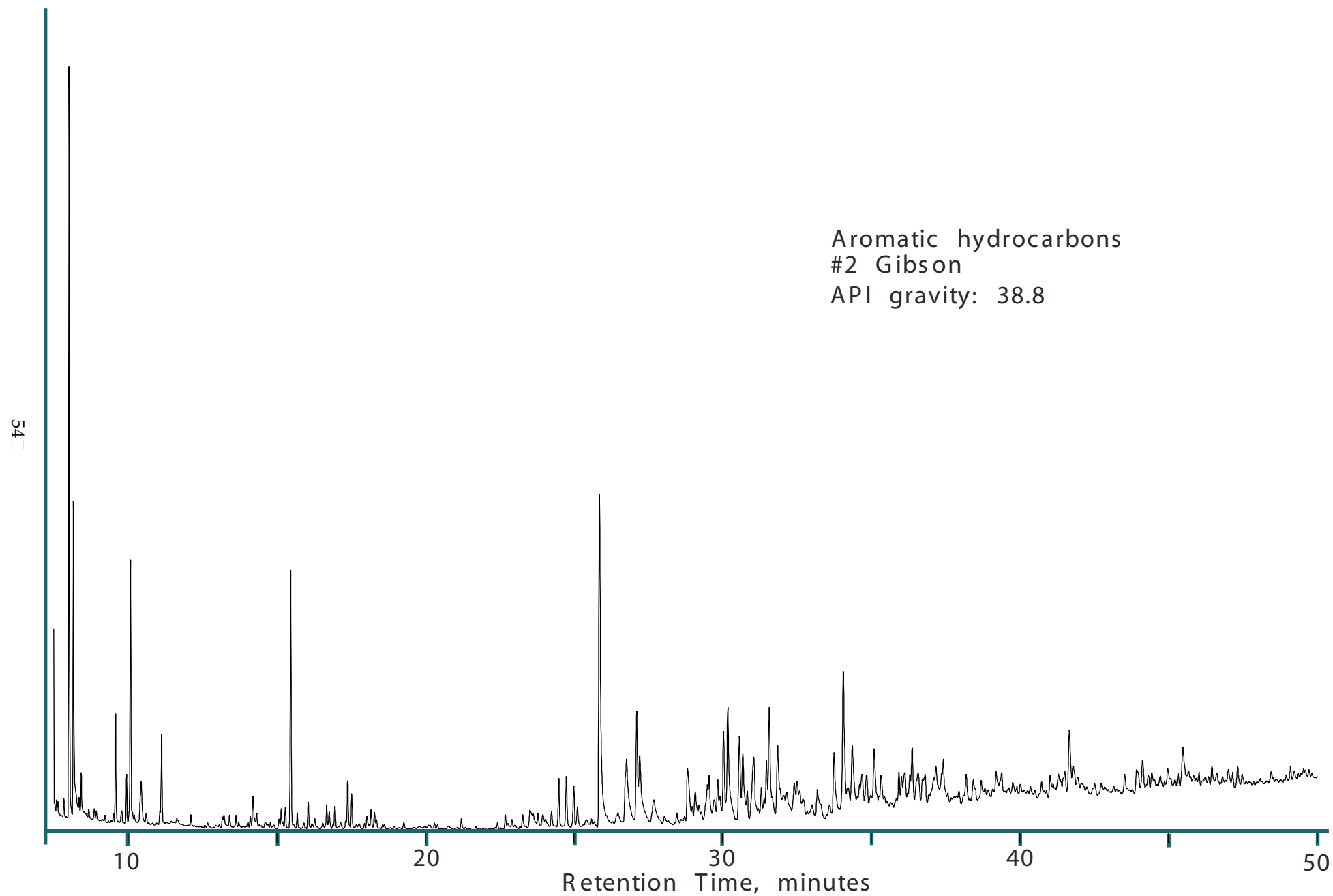


Figure 15C: Aromatic hydrocarbon fraction gas chromatogram, sample 98PA06A, #2 Gibson.

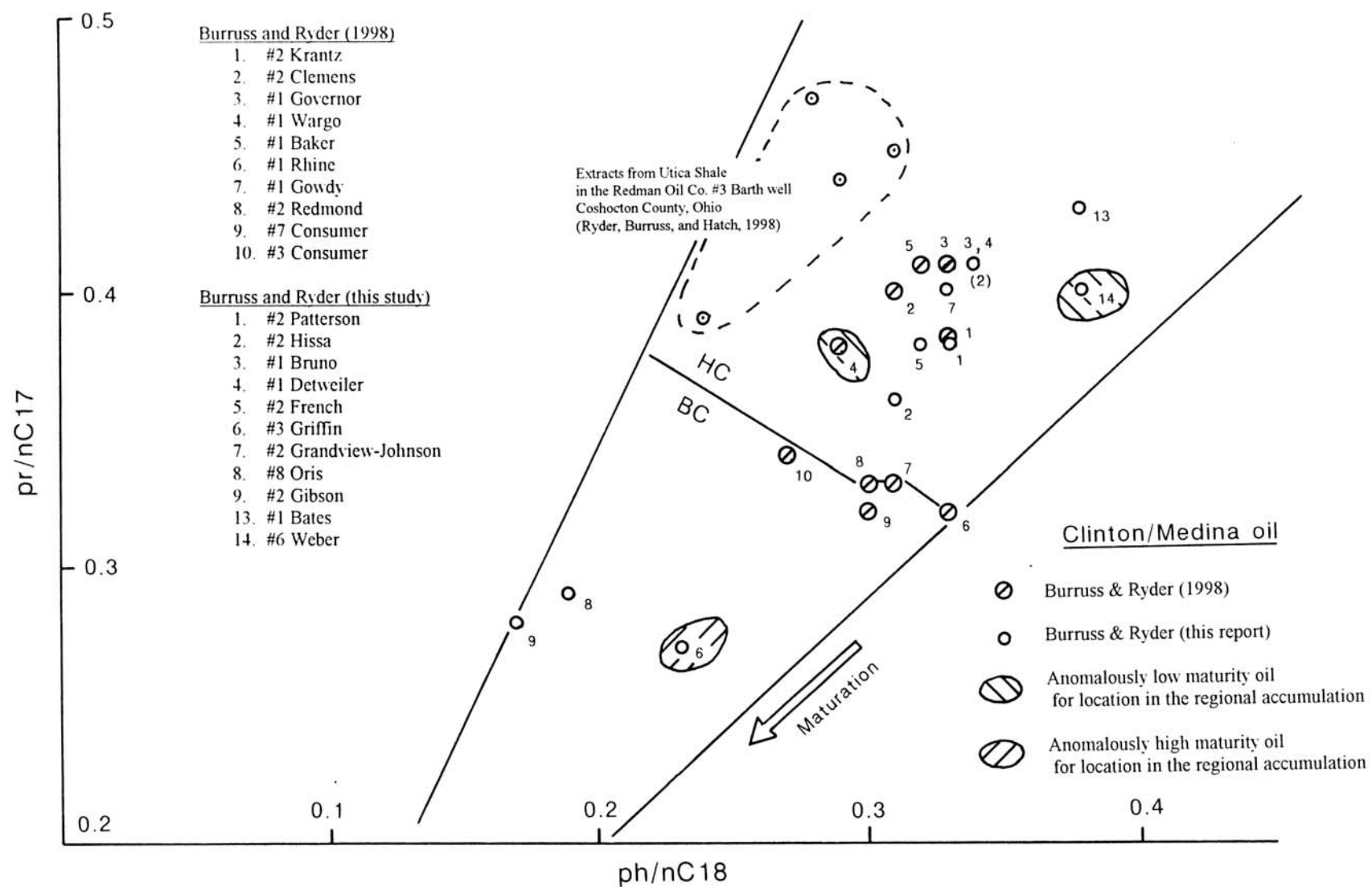


Figure 16. Plot of $pr/nC17$ vs. $ph/nC18$ for "Clinton"/Medina oils and Utica Shale bitumen extracts. BC - Basin-center part of the regional accumulation; HC - Hybrid-conventional part of the regional accumulation.

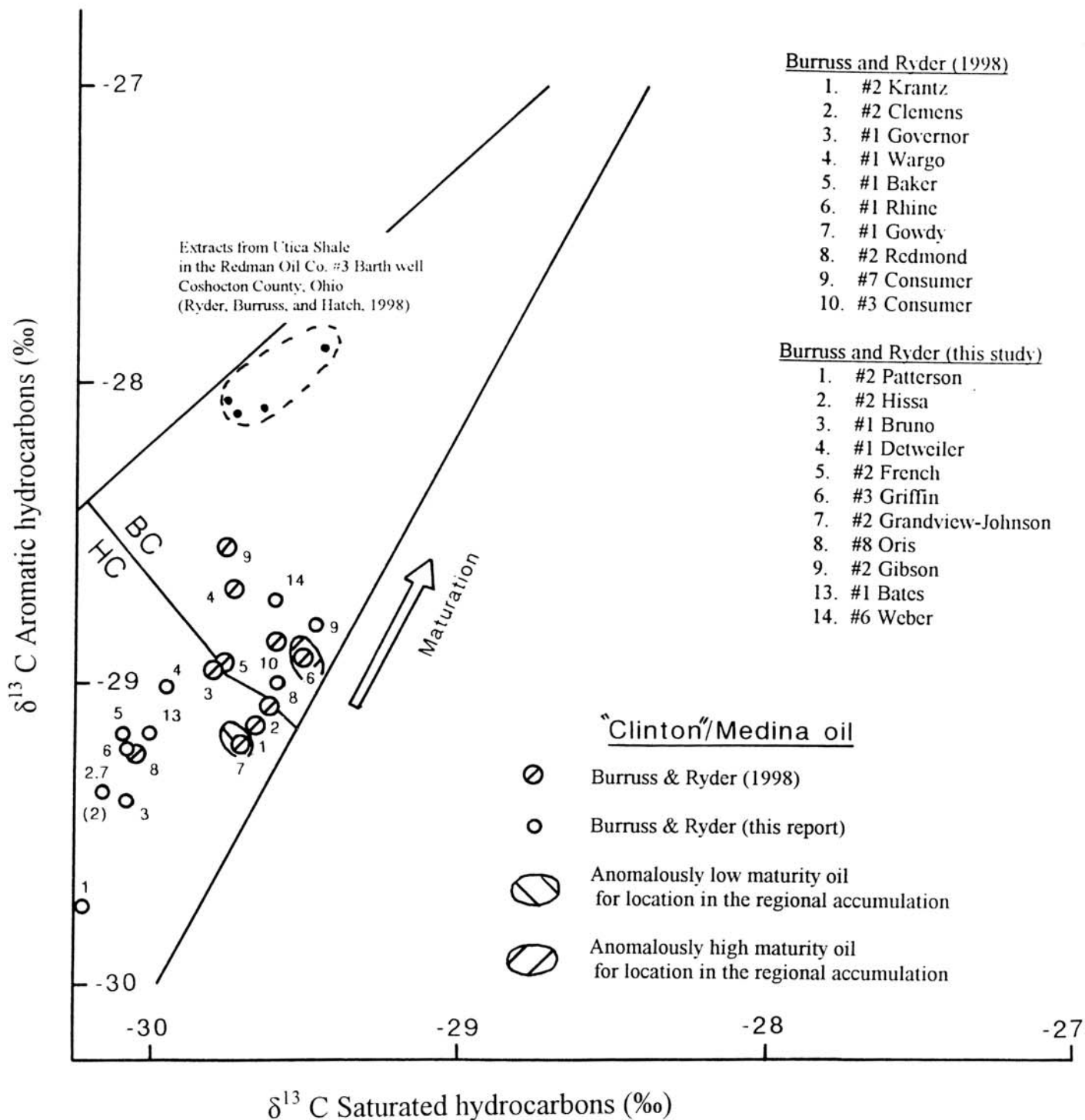


Figure 17. Plot of $\delta^{13}\text{C}$ distributions in the saturated and aromatic hydrocarbon fractions for "Clinton"/Medina oils and Utica Shale bitumen extracts. BC - Basin-center part of the regional accumulation; HC - Hybrid-conventional part of the regional accumulation.

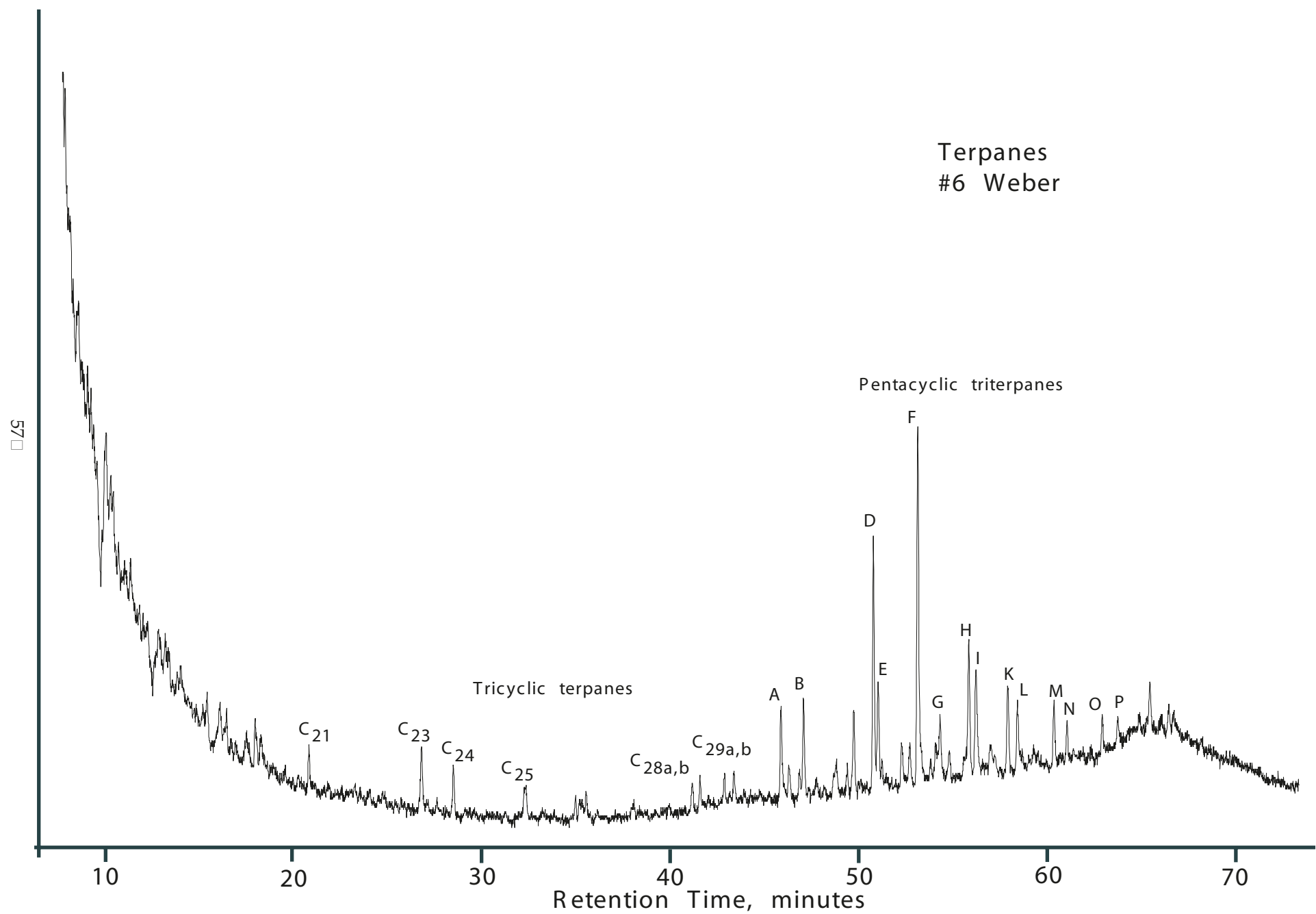


Figure 18A: Terpane mass fragmentogram, m/z 191.180, sample 98PA02, #6 Weber.

58 □

Steranes
#6 Weber

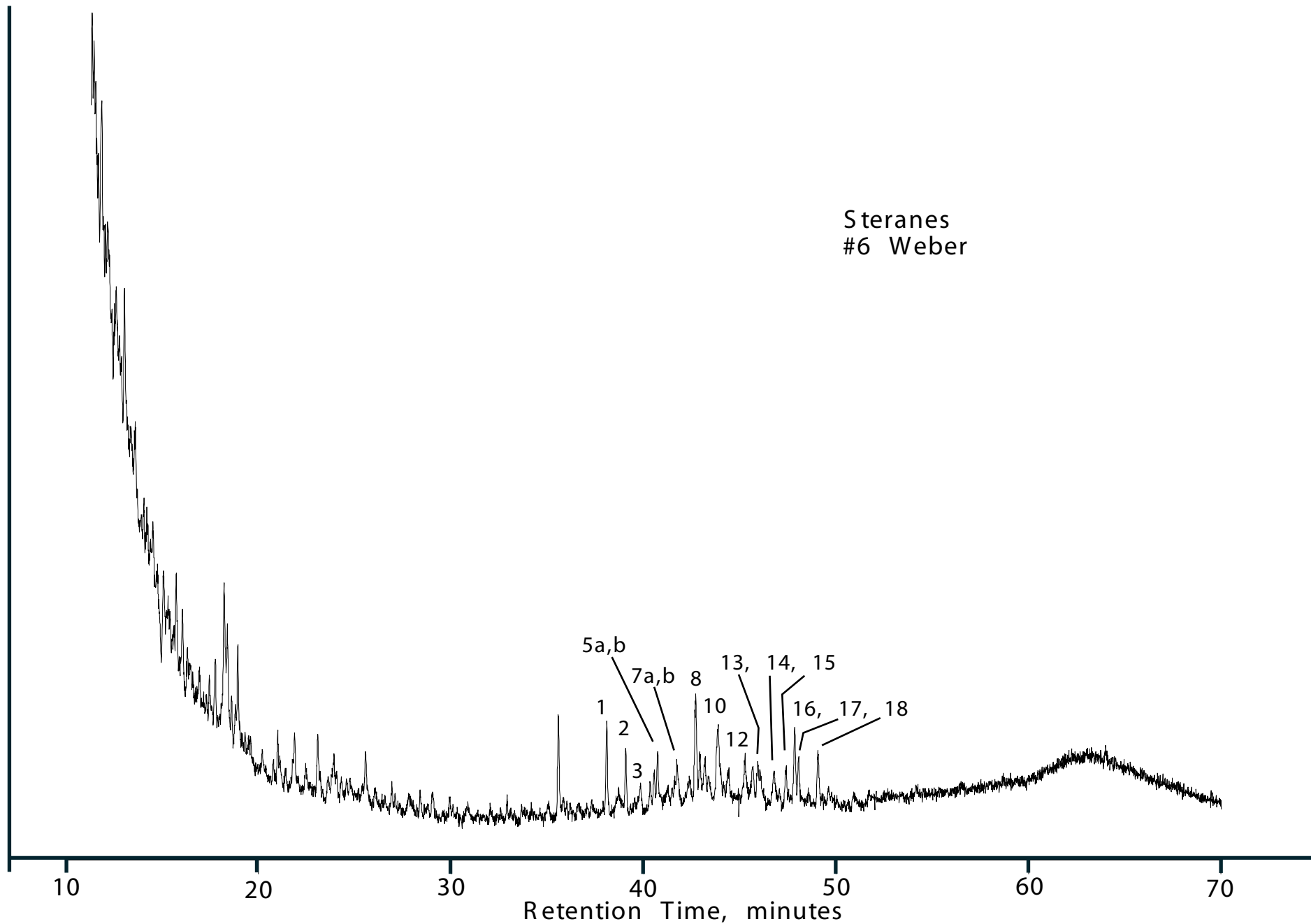


Figure 18B: Sterane mass fragmentogram, m/z 217.1956, sample 98PA02, #6 Weber.